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AUTOMATIC ORGANIC MONITORING SYSTEM FOR STORM AND COMBINED SEWERS

Angelo Tulumello

Raytheon Company

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AUTOMATIC SAMPLING STATION FOR STORM AND COMBINED SEWERS

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Early in the program to develop a stormwater TOC (total organic carbon) system, it was established in report EPA-670/2-74-087 that continuous on-line TOC was the best method for the measurement of stormwater pollution loading. Hardware was assembled that would process stormwater samples containing high suspended solids and that would obtain a continuous signal proportional to the concentration of TOC in the sample.

Synthetic samples of municipal raw influent charged with primary sludge were analyzed using the TOC analyzer. Data were also obtained on actual stormwater samples collected during storm events at Boston. Further modifications were made after these observations.

Automatic circuitry designed to provide turn on, auto-zero, auto-span and sample line flushing was added to the hardware, and the system was installed at Boston Cottage Farm Storage Facility.

Automatic continuous analyses were obtained during storms on site at the Cottage Farm Storage Facility.

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AUTOMATIC ORGANIC MONITORING SYSTEM FOR STORM AND COMBINED SEWERS

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Contract No. 68-03-0262
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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise, and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment—air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in:

- studies on the effects of environmental contaminants on man and the biosphere
- a search for ways to prevent contamination and to recycle valuable resources.

This report discusses the development and evaluation of an automatic monitoring system for measuring organics in storm and combined sewage. Total organic carbon measurement was found to be the optimal method for measuring storm-generated pollution.

A.W. Breidenbach, PhD
Director, National Environmental
Research Center, Cincinnati

ABSTRACT

Early in the program to develop a stormwater total organic carbon (TOC) system, it was established in report EPA-670/2-74-087 that continuous on-line TOC was the best method for the measurement of stormwater pollution loading. Hardware was assembled that would process stormwater samples containing high suspended solids and that would obtain a continuous signal proportional to the concentration of TOC in the sample.

Synthetic samples of municipal raw influent charged with primary sludge were analyzed using the TOC analyzer. Data were also obtained on actual stormwater samples collected during storm events at Boston. Further modifications were made after these observations.

Automatic circuitry designed to provide turn on, auto-zero, auto-span, and sample line flushing was added to the hardware, and the system was installed at Boston Cottage Farm Storage Facility.

Automatic continuous analyses were obtained during storms on site at the Cottage Farm Storage Facility.

This report was submitted in partial fulfillment of Program Element No. 1BB034, Contract No. 68-03-0262 by Raytheon Company under the sponsorship of the U.S. Environmental Protection Agency. Work was completed in March of 1975.

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We also wish to acknowledge the cooperation of Mr. Allison C. Hayes, Director of the Sewage Division of the Metropolitan District Commission of Boston for allowing us to install our instrumentation at the Cottage Farm Storage Facility. In addition, we wish to express our appreciation of the cooperation of Mr. Frank Zinfolino, Manager and his staff of the Cottage Farm Storage Facility who provided us the necessary operating information and assistance in the installation of hardware and the assembly of operating data.

SECTION I

CONCLUSIONS

1. The total system for the evaluation of storm-generated pollution depends upon the availability of a sample delivery system and a suitable processing and analysis system. A sample processing and analysis system has been described. A suitable sample delivery system is yet to be designed. At the present stage of development, each location must have a custom sample delivery subsystem.

2. Total organic carbon (TOC) analysis is a rapid, reliable and well-correlated method for measuring storm-generated pollution.

3. A stormwater TOC measuring system has been developed and field tested.

4. The stormwater TOC measuring system can be calibrated on potassium acid phthalate (KHP) in accordance with the method of the Environmental Protection Agency.

5. Tests at the Boston Metropolitan District Commission-Cottage Farm Combined Sewer Overflow Storage Facility (Cottage Farm Storage Facility) indicate that the installed system assembly is capable of accurately monitoring TOC of storm-generated pollution.

6. Unattended and automatic turn on, turn off, auto-zero, auto-span, and the sample delivery flush systems eliminate the need for frequent operator attention and permit continuous on-line readiness.

7. Manhole installation of the TOC instrumentation presents substantial problems. The present equipment, placed in a mobile or remotely located trailer or a shed operation, can be expected to collect reliable data from a suitably designed sample delivery system.

8. The cost of stormwater TOC instrumentation cannot be realistically estimated at this time because the cost of a practical sample delivery subsystem is unknown. The cost of the stormwater TOC instrument without sample delivery subsystem is about one and a half times the cost of the present online TOC instruments available for other purposes.

9. The reliability of the stormwater TOC instrument exclusive of the sample delivery subsystem is adequate to the needs of stormwater control and treatment applications.

SECTION II

RECOMMENDATIONS

1. Verify the existing system with further wet-weather testing at some on-going USEPA demonstration project where comparative data are desired. This would include an improved sample delivery subsystem.
2. Determine control and treatment strategies utilizing the combined system at selected sites.
3. Incorporate feed-forward control and exercise the system by utilizing the developed control strategies.
4. Specify and deploy stormwater control and treatment systems based on the preceding steps.

SECTION III

INTRODUCTION

THE PURPOSE OF THE DEVELOPMENT

One of the major sources of pollution of our natural bodies of water is the random occurrence of uncontrolled storm flows in both storm and combined sewer facilities. Programs of stormwater diversion, detention, and treatment have been suggested as a means of controlling these events.

The nature of a storm flow presents a characteristic system loading as a function of time. The first effect of the high velocity turbulent flow of water is to scour the drainage area, cleaning the ground of organic material (leaves, grass, asphalt), and suspending settled solids that have come to be deposited in the sewer system. This flow entrains a rich and concentrated organic load which cleans as it flows. Later flow may act to dilute the remaining pollution load.

To implement a timely course of action in handling this pollution source it is necessary that one obtain a real-time measurement of the pollution level of the storm flow. The information resulting from this measurement can be used in the control and treatment of stormwater, in system design programs, or for enforcement purposes.

The purpose of this contract is to develop and demonstrate an efficient automatic monitoring device for the rapid, in situ determination of dissolved and suspended organic loading. Several options were available in developing a suitable analytical scheme to monitor the pollution level of storm flow: biological oxygen demand (BOD), chemical oxygen demand (COD), total oxygen demand (TOD), or total organic carbon (TOC). After a careful evaluation, TOC was selected for development.

The Choice of TOC

Storm flows present a highly variable sample containing a wide variety of organic materials in various forms, among these is a first flush of high concentration of suspended solids. This presents a particularly severe sample from which to obtain essentially instantaneous data. TOC was recognized as the only practical analytical technique that could deliver the quantitative information necessary to permit rapid, intelligent, and appropriate action that could be used to interface with the facilities used to handle the pollution load. The TOC analysis is a relatively independent analysis requiring a minimum of maintenance and supply—this is not true of wet chemical and biological systems. Because of this, it is possible to enclose the system in a mobile or sheltered enclosure.

Instrumentation Considerations

The problem associated with the adaptation of chemical analyses to on-line monitoring is not the ability to assemble hardware that will perform the required operations. The main problem is to keep the hardware operating reliably in time. Chemical systems dependent on convection to go to completion tend to have a relatively long reaction time. The conditions that chemical systems present are limitations to the hardware normally used to transfer solids, liquids, and gases. The need for acids, bases, and other reactive reagents, and the requirement of high temperature and pressure places severe strain on materials used in sample handling. As a result of these conditions, materials and designs have to be carefully selected and tested to provide the reliability required for action based on continuous on-line analyses.

The operating conditions for continuous on-line monitoring instrumentation are much more severe than those normally imposed on laboratory equipment. Laboratories provide ready and experienced service when breakdown occurs. When on-line instrumentation fails, it interrupts an established routine which places a random strain on the available service personnel. This frequently occurs when other pressing assignments are in process, resulting in a prolonged period of downtime for the instrumentation. Under conditions of this kind, people lose their confidence in the reliability of the hardware and often disarm it.

Modern material technologies have provided us with previously unrealized options in addressing the conditions necessary for continuous on-line chemical analyses. Quantitative peristaltic pumping provides us with a considerable improvement in sampling suspended solids. Inconel alloy provides the high temperature furnace environment required for a complete combustion and long service. The reliability of modern solid-state switching, the availability of off-the-shelf tube connectors and the versatility and improvement in modern plastics has made it possible to assemble and test the hardware necessary to perform the continuous on-line analysis of TOC in stormwater.

The design of instrumentation for the analysis of stormwater and combined sewage presents problems which result from the nature of the sample. The sample contains solids as well as liquid in several phases (i.e., oil in water). This requires care in sample transfer to minimize fiber hang-up and solids coagulation sites that can occur in low velocity delivery systems. The plumbing can provide sites for solids collection and plug formation. These sites can be minimized by transferring sample through carefully assembled sanitary (connections without shoulders) fittings. These problems were addressed in Phase I.

The above mentioned problem areas, made it necessary to plan an on-line field test and to provide a program of vigorous routine maintenance with documented experience and redesign as indicated by the field experience. In this way, it was possible to demonstrate the reliability of Raytheon's instrumentation for installation in continuous on-line monitoring of storm flows. This was done in Phase II.

SECTION IV

PHASE I—REVIEW

During Phase I, a report was prepared entitled an "Assessment of and Development Plans for Monitoring of Organics in Storm Flows", EPA-670/2-74-087. It is appropriate to review some of the material contained in the report and see how it would apply to the system employed in the laboratory portion of Phase I.

In compiling this report, several criteria were established for the judgment of the hardware. The optimal system would be one which would operate reliably and reproducibly in the concentration range-of-interest (5 to 1000 mg/l TOC). It should require a minimum of maintenance, be economical, and operate under conditions likely to be found in a storm flow sewer or control facility. The devices should be automated as to zero, span, startup and shutdown. In addition, the storm flow TOC monitoring system should be capable of analyzing samples with varying suspended solids concentrations.

These requirements are necessary to perform efficient organic carbon analyses at remotely located storm sample sites. They have been recognized and defined in the design goals of this contract.

Continuous operating on-line TOC analyzers have not, in general, been able to meet these requirements. The common problems encountered in the experimental effort have been substantial. The delivery of a continous representative sample containing up to 1000 mg/l suspended solids is a considerable accomplishment. The continuity of the delivery is easily interrupted because of plugging. These problems tend to render unreliable much of the commercial hardware designed to process and deliver representative samples containing suspended solids. If suspended solids are removed, the samples are not representative and the TOC measurements are unreliable. Care must be taken in the design of systems of continuous TOC analysis to reduce the particle size, transfer the particles, and deliver them through sanitary fittings to an efficient and continuous analytical system.

STATE-OF-THE-ART

The commercially available, continuous duty TOC instruments have a demonstrated history of failure; moreover, their maintenance requirements are so substantial that some of the instruments have been abandoned. The problems associated

with the design of TOC instrumentation of this type are not only the problems of sample delivery but also the difficulty of providing efficient continuous combustion of small amounts of carbon in water. In order to accomplish this, it has been shown that a high temperature, 950° C, is needed so that compounds delivered to the reactor may be oxidized rapidly regardless of the nature of the organic structure of the material. This is a problem of some magnitude in itself. Many of the instrument suppliers have cascaded their difficulties by incorporating flame ionization detection (FID) and catalytic reactors. These have their own failure modes and tend to add to the unreliability of the instrumentation.

A review of the literature indicated a need for a continuous TOC analyzer. The TOC technique has several advantages over the alternative methods of organic pollution monitoring, BOD and COD. BOD and COD are both time consuming. BOD is non-reproducible. They are dependent upon operating conditions and the nature of the sample. TOC can be specific to organics; it is very reproducible. Operating instrumentation can provide essentially real-time data in time to take necessary action.

Storm events place excessive and unpredictable organic loads on sewage facilities. With consideration of the storm events and the problems associated with processing samples during these events, a stormwater TOC system was proposed for the TOC analysis. This system is diagrammed in Figure 1. The validity of the proposed TOC system was verified in an extensive laboratory test program which included both simulated and actual stormwater samples.

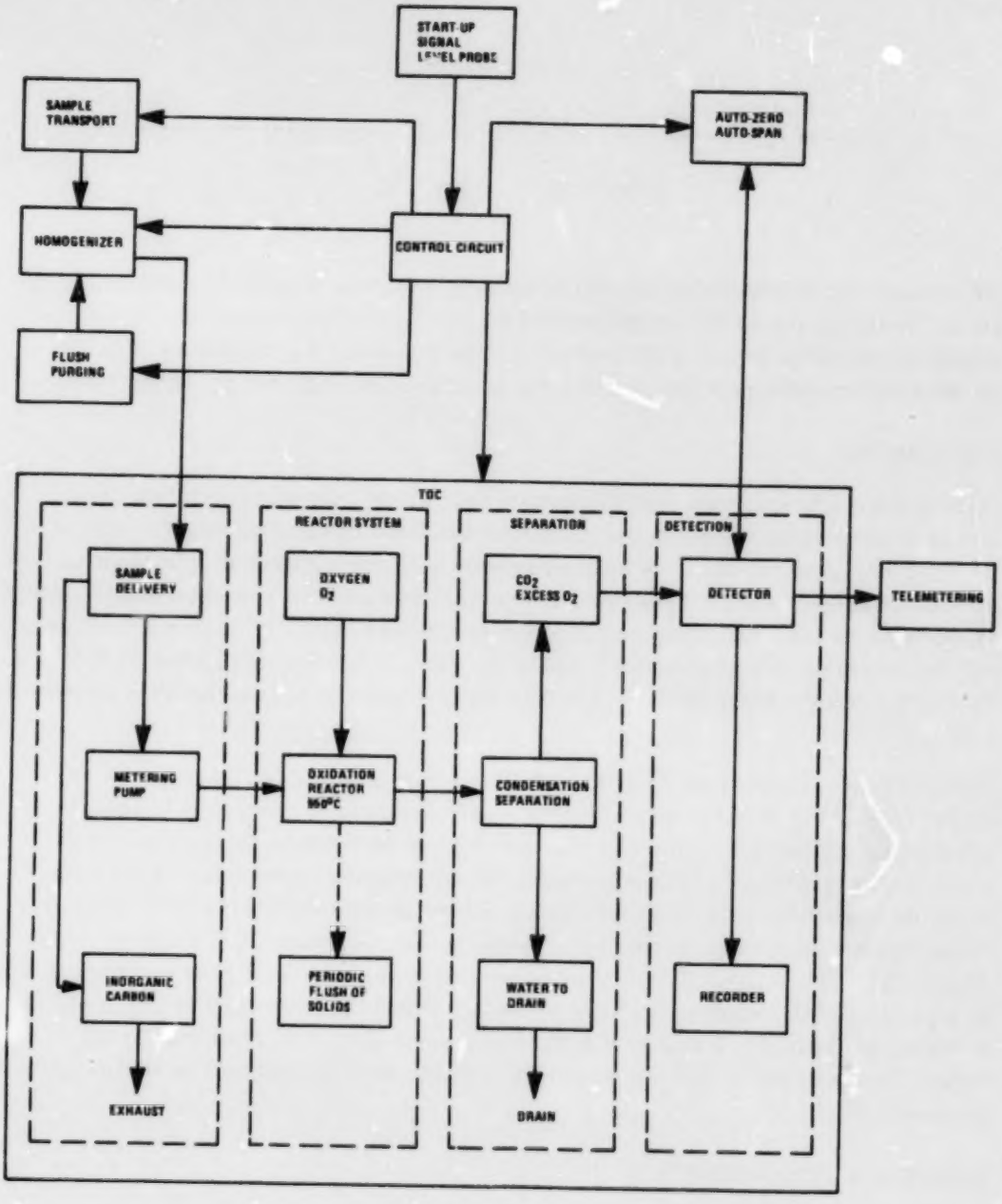


Figure 1. Stormwater TOC system, block diagram

SECTION V

EXPERIMENTAL WORK

To discuss the performance of a TOC system, certain standards must be established to demonstrate the experimental results. This section of the report, presents the substantiating data necessary to demonstrate the device's ability to meet the requirement for on-line measurement of organics in storm flows.

PROCEDURE

During the early stages of the laboratory test effort, simulated stormwater samples were used to obtain the performance data. The simulation of stormwater runoff and combined sewage overflows was accomplished by adding settled primary sludge, containing about 25,000 mg/l of solids to raw municipal sewage resulting in a net TOC of 500 mg/l and a suspended solids of 1000 mg/l. Later in the program, actual combined sewer overflow samples, collected from Boston's Cottage Farm Storage Facility were used to evaluate the TOC system's performance.

The equipment used in these simulated tests consisted of an assembly of hardware designed to deliver representative samples from a sample container by careful control of flow rates and the delivery of the sample through properly sized sanitary fittings. The simulated storm samples were delivered continuously through the Raytheon homogenizer (Refer to EPA-670/2-74-087, Page 41) from which a continuous stream was taken to the Raytheon TOC analyzer (see Figure 2). The sample delivery system is diagrammed in Figure 3. Figure 4 is a picture of the sample delivery system. The hardware used in the application is listed in Table 1. Prior to discussing the results, it is first necessary to define the accuracy and precision of the system and the methods of defining these parameters.

ACCURACY AND PRECISION

The accuracy of an instrument can be established by reference to the precision with which the instrument analyzes primary standard solutions of a known composition. In this case, the method of the EPA (USEPA Publication No. 16020—07/71, Pages 221-229) is specified by contract. This method employs a Beckman TOC analyzer, whose precision depends strongly on the sample characteristics,

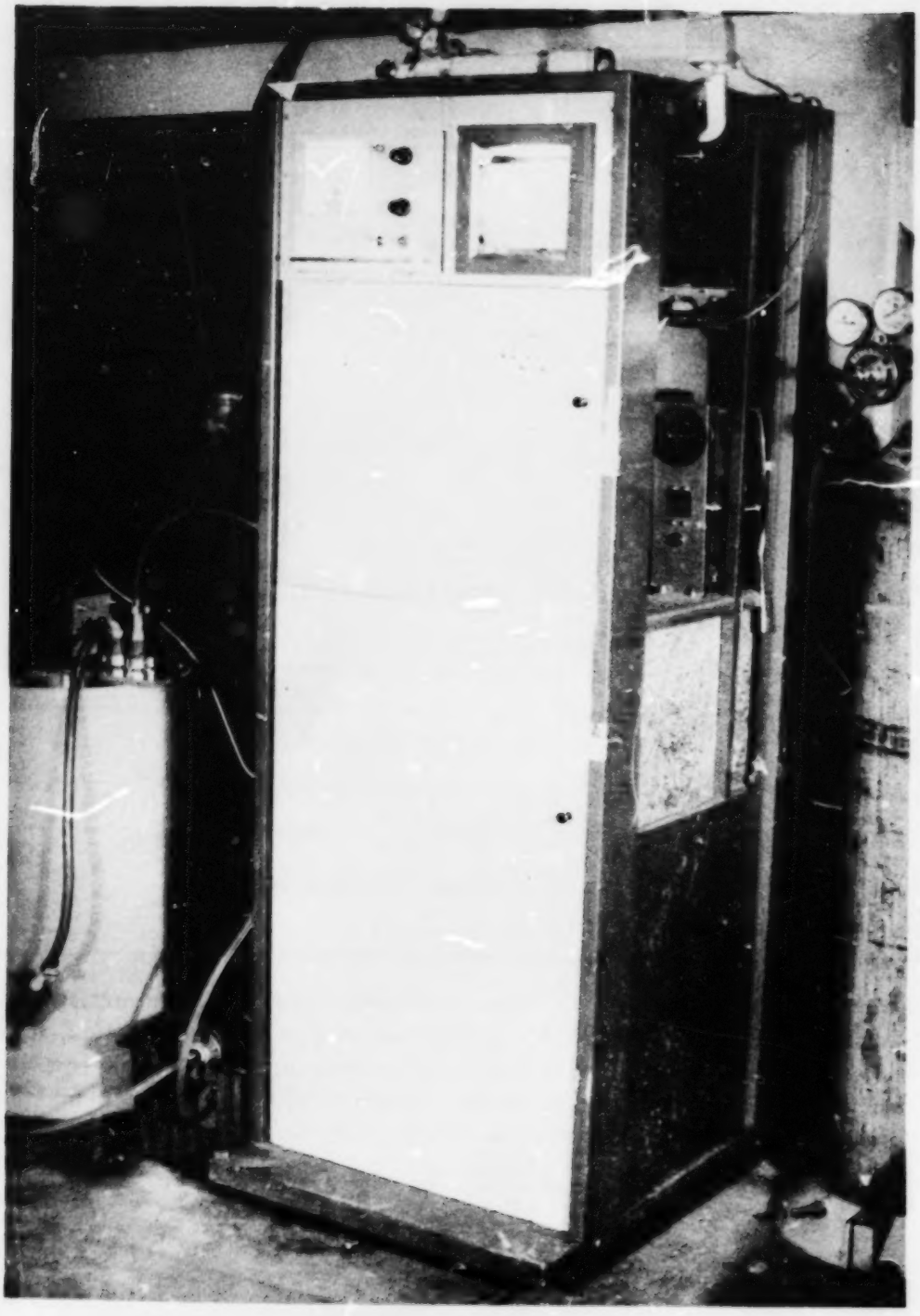


Figure 2. Raytheon TOC

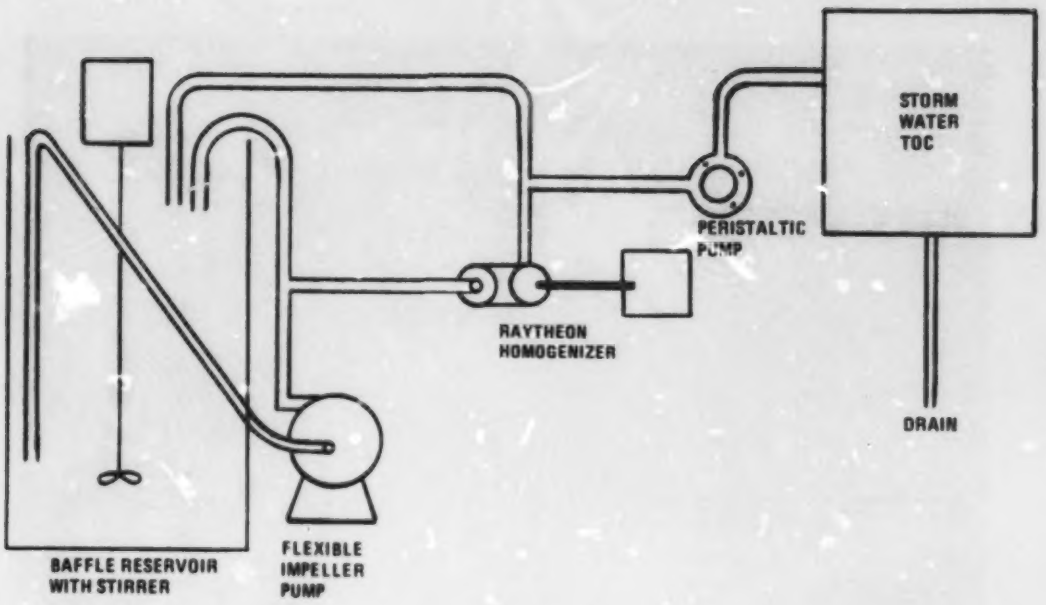


Figure 3. Sample delivery system for simulated laboratory tests

Table 1. HARDWARE USED IN STORMWATER SIMULATION

Function	Hardware
Container	50-gallon Fiberglas Drum
Motor Driven Stirrer	1/20 Horsepower Industrial VWR Stirrer
Sample Delivery Pump	Barnat Variable-Speed Peristaltic Pump
Particle Reduction	Raytheon Homogenizer
TOC Analysis	Raytheon TOC

specifically on the type, concentration and preliminary treatment of the suspended solids. To obtain data of any value at all with suspended solids, it is necessary for the discrete sample to be processed through a Waring type blender until the biggest particle can be passed through a 0.02 inch needle in both directions without coalescing on the walls of a 20 μl syringe.

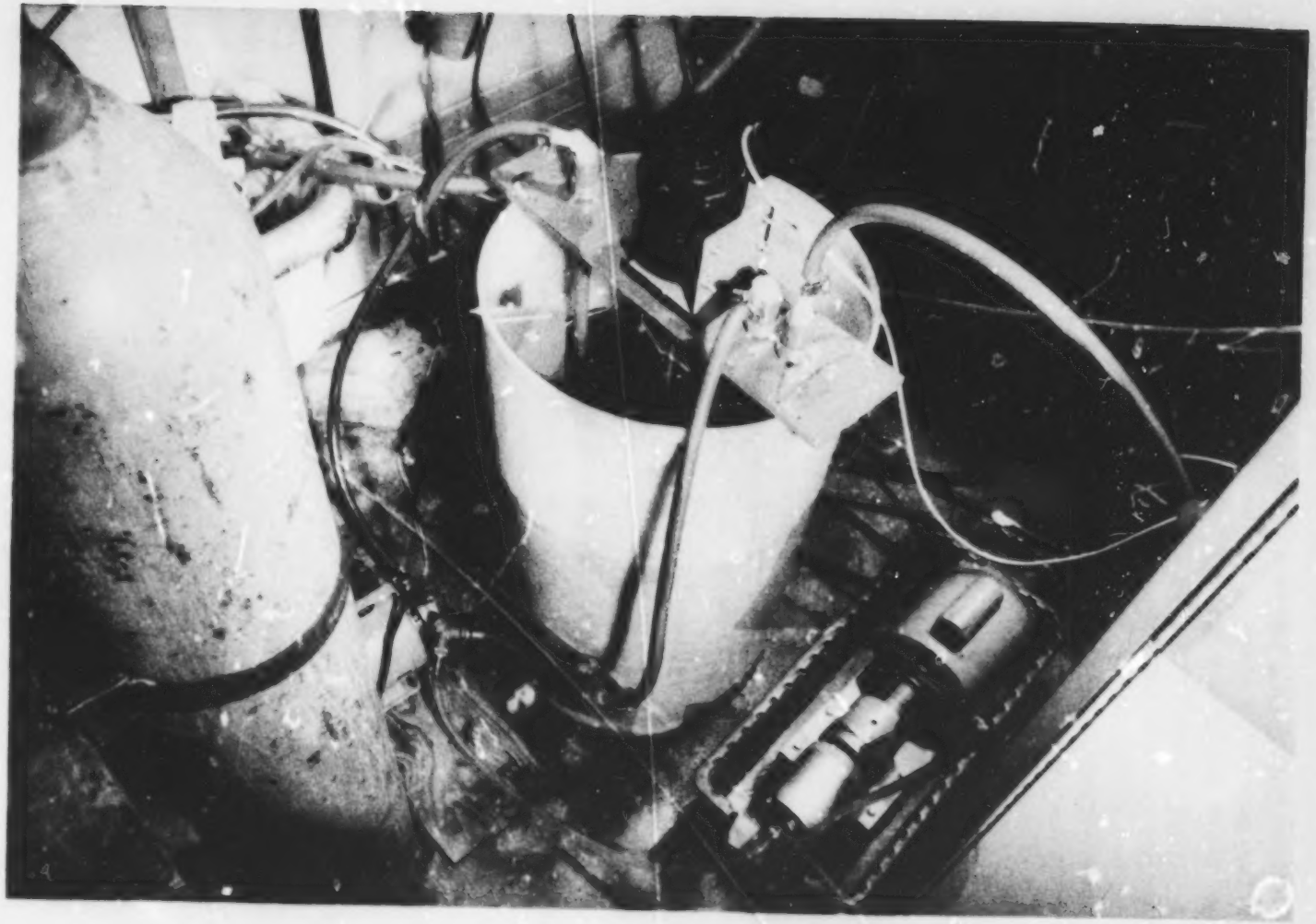


Figure 4. Simulated stormwater delivery system

The Raytheon TOC, like the Beckman TOC, is standardized, by generating a TOC signal from a solution of known composition of a primary standard. The material used to prepare these standards is potassium acid phthalate (KHP). Using this material, a scale is established to operate in the concentration region-of-interest to stormwater analysis (0-1000 mg/l). Because the Raytheon TOC has a continuous delivery system, the signal obtained does not depend on the precise selection, measurement, and delivery of a discrete sample containing solids, but delivery occurs continuously with time. If organic solids are delivered to a continuous analyzer, a high reading will appear for the period during which the sample is being processed. The precision and accuracy of the instrument is established by burning clear solutions of known composition.

When an instrument has been designed for measurement over a concentration range, it is not generally used over a very different concentration range without modification. The stormwater TOC was intended to operate from 0-1000 mg/l. The error expected in any measurement with this instrument is ±2% of full scale. Reference samples were submitted by the EPA Analytical Quality Control Laboratory. It was established that the concentration of the more concentrated of these samples was 140 mg/l TOC; the lower concentration was 4 mg/l TOC. Data collected at this lower concentration are within the expected instrumentation error and could not practically be measured with the stormwater TOC assembly.

In order for an analytical technique to be of any value to the operators, it is necessary to have some estimate of the error associated with the application of the technique to the problems at hand. This error can be assumed to be associated with a normal spread of the data obtained for a particular true value of an aliquot which can be estimated by identifying each mean value with a standard deviation, "s". Small standard deviations result when the techniques are capable of precise estimation of the values-of-interest. Soluble TOC is not difficult to determine by any TOC analyzer. The EPA reports standard deviations of the order of 8 mg/l on soluble organics with concentration of 107 mg/l. The stormwater TOC analyzer has done somewhat better than this throughout the range of soluble TOC. This is true with both filtered biological materials as well as with KHP.

Most continuous TOC analyzers have difficulty in the combustion of KHP because of the noise which results from the nonuniformity of combustion of this species. To avoid these problems, secondary standards have been used (for example, sucrose and ethylene glycol) as reference solutions because of their greater ease of combustion. These secondary standards have been prepared by a previous comparative analysis using KHP.

In the stormwater TOC system, as in the standard method of the EPA, a solution of KHP may be burned directly as a primary standard. This has been accomplished by establishing a more efficient combustion chamber. Higher temperature (950° C) and smaller sample size (2 cc/min) were found to give efficient combustion of 425 mg/l TOC prepared from KHP.

The combustion of suspended solids is a considerable accomplishment in itself. In the TOC method of the EPA, it is suggested that "insoluble particulate carbonaceous materials" can be analyzed using the Beckman TOC. However, there is no precision data associated with this analysis. A little experience with this technique shows that there is considerable difficulty in obtaining very precise data. The solids themselves are variable as are the combustion characterisitcs of the possible components in the stormwater system. This type of sample results in an unpredictable variability that can be expected to be at least twice that of the soluble TOC values.

Raytheon has demonstrated considerable success in the efficient combustion of suspended solids as will be noted in the following section describing the stormwater results.

STORMWATER RESULTS

Simulated Storms

A sample data sheet obtained with a synthesized storm is seen in Table 2. In establishing a simulation of storm sewer loading it becomes necessary to

Table 2. COMPARISON DATA OBTAINED FROM SIMULATED STORM CONDITIONS

Characterization Sample		In Batch Tank				Delivered to TOC			
		Primary Effluent	(A) +800 ml Primary Sludge	(B) 50% Dil of (A)	50% Dil of (B)	Primary Effluent	(A) +800 ml Primary Sludge	(B) 50% Dil of (A)	50% Dil of (B)
		Sample 21	Sample 22	Sample 23	Sample 24	Sample 21A	Sample 22A	Sample 23A	Sample 24A
Stormwater Mean TOC Standard Deviation						113.5	456.8	193.1	110
						1.73	49.7	7.6	5
Beckman TOC mg/l	1	130	425	190	90	115	470	180	95
	2	115	425	185	90	110	450	175	95
	3	120	420	190	90	110	470	170	95
	4	120	425	185	105	115	480	175	90
	5	120	425	185	90	115	480	180	100
	Mean	121	426	187	93	113	466	176	95
Std Deviation		5.48	2.24	2.74	6.71	2.74	11.4	4.18	3.5
Settleable Solids	30 Min	1 ml/l	50 ml/l	12 ml/l	2 ml/l	NR	NR	NR	NR
Suspended Solids mg/l		120	1,090	390	140	110	1,070	360	200
Particle Size Distribution mg/l	420μ	6.5	209	40	12	1	122	53	9
	210μ	9	16	9.5	5	0	21	4.5	1
	110μ	11	15	4	5	0	18	11	5

Condition at the time of data collection
Peristaltic by-pass flow rate 900 cc/min
Raytheon homogenizer flow rate 800 cc/min

rapidly add a high concentration of suspended solids to a rather modestly loaded (200 mg/l TOC) sanitary sewage. This increases the concentration of TOC to about 500 mg/l TOC. This also increases the severity of the combustion required to produce rapid complete oxidation. The easiest solids to burn are those that contain fairly large amounts of water structurally bound to the carbon.

Hydrated pulps make the most easily handled suspended solids for TOC analysis. Items such as plastics, rubber, and carbon structures that have survived ultraviolet radiation, biological degradation, rain, abrasion, and high and low temperatures are among the most difficult to combust in continuous analyses. Storm flows tend to concentrate the more resistant structures. Municipal sewage tends to contain more hydrated pulps, but combined sewage in general is a random mixture of all of these. As a result, there is always some level of nonuniformity to the combustion of suspended solids.

To minimize nonuniform combustion, it was found that it is desirable to grind the suspended solids to a size no larger that 1200 microns in largest dimension and deliver them rapidly, uniformly, and quantitively to an efficient combustion environment.

Our first synthesized storms were prepared by adding primary sludge to primary effluent. This was a conveniently random sample on which to optimize our delivery system. Solids loading established in this way was very severe. The data obtained showed standard deviations which were large compared to similar data obtained using the Beckman analyzer and a Waring blender, as shown in Table 2.

Table 2 is a presentation of data collected on four sewage samples delivered to the stormwater TOC assembly. The purpose of this experiment was to show that sample had been delivered to the continuous analyzer in such a way as to retain a concentration of TOC at the continuous analyzer that was representative of the material in the batch tank (see Figure 3). If the sample delivery system is properly assembled, the TOC values in the batch tank sample, as measured by the Beckman TOC unit will be found to be essentially the same as the Beckman TOC values obtained on samples from the exhaust of the Raytheon homogenizer. These in turn will be essentially the same as the sample analyzed on the continuous analyzer. In order to simulate a storm loading condition, four compositions are examined. The first is primary effluent which is characterized and analyzed as seen under primary effluent. This sample is then enriched with primary sludge to represent the sewer loading associated with the first flush effect. We can see that the solids loading has increased with the increase in TOC and that there has been considerable reduction in the total weight of the larger particles because of their treatment in passing through the blender even though the suspended solids

remain essentially the same. The next two samples show the result of water additions to the enriched primary effluent, simulating the later stages of storm flow.

The mean and standard deviations of the discrete TOC samples are obtained by a simple calculation using the numbers the table. The standard deviations of the continuous data are obtained by selecting sample data from the continuous recording. It was found that in these data, and similar tables of data, that the standard deviation is proportional to the concentration of suspended solids.

Actual Stormwater Samples

In some actual stormwater samples obtained during storm flows at the Cottage Farm Storage Facility, the problem of the nonuniform combustion of suspended solids became even more severe; in others it was not. Since there is a concern with the general condition of stormwater, it became necessary to improve the combustion environment so that the more severe samples might be uniformly combusted. To do this, operating modifications were necessary to minimize the removal of heat from the reactor, close to the point of sample delivery. The flow rate of water at the sample delivery tube was minimized. This minimized the loss of heat through this medium. The effect of this operation was to decrease the nonuniformity of the combustion, and consequently minimize the noise in the signal from samples containing high suspended solids.

Data taken on flows during the storm of April 23 seemed quite acceptable. Storm samples collected during the storms of May 10 and 12 gave a very different picture. The difference was probably caused by the fact that on 4/23/74 much of the carbon was present as soluble material. See Figure 5, Table 3 and Figure 6 for the storm of April 23; Figure 7, Table 4 and Figure 8 for the storm of May 10 and Figure 9, Table 5 and Figure 10 for the storm of May 12. In the case of the storms of 5/10/74 and 5/12/74, the soluble organic carbon is very low, approaching the concentration of organic carbon in deionized water (10 mg/1). The suspended solids are quite high and contain virtually all the organic material. As a result, the signal is noisy even in samples that have a relatively low TOC. A study of these data indicate that stormwater is a more severe sample than the simulated sample in which primary sludge is added to primary effluent. This is probably because of the fact that primary sludge consists largely of hydrated pulps and stormwater organic solids contain more resistant carbon structures.

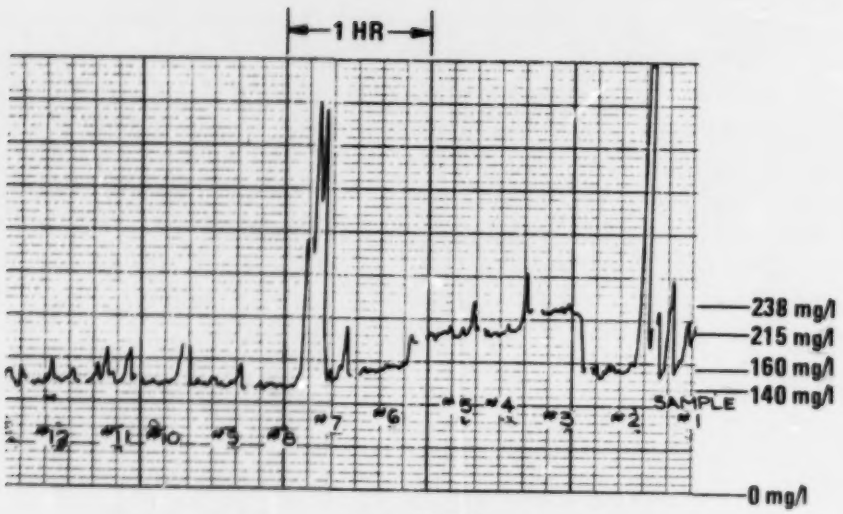


Figure 5. TOC chart for the storm of 4/23/74

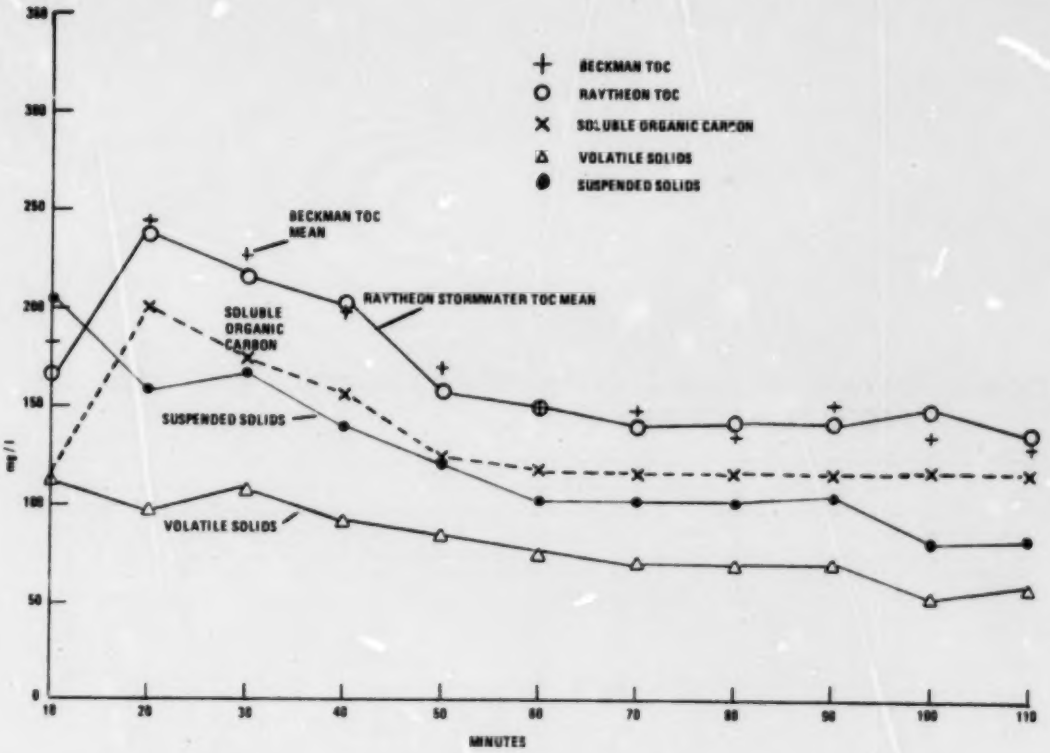


Figure 6. Characterization of the storm of 4/23/74

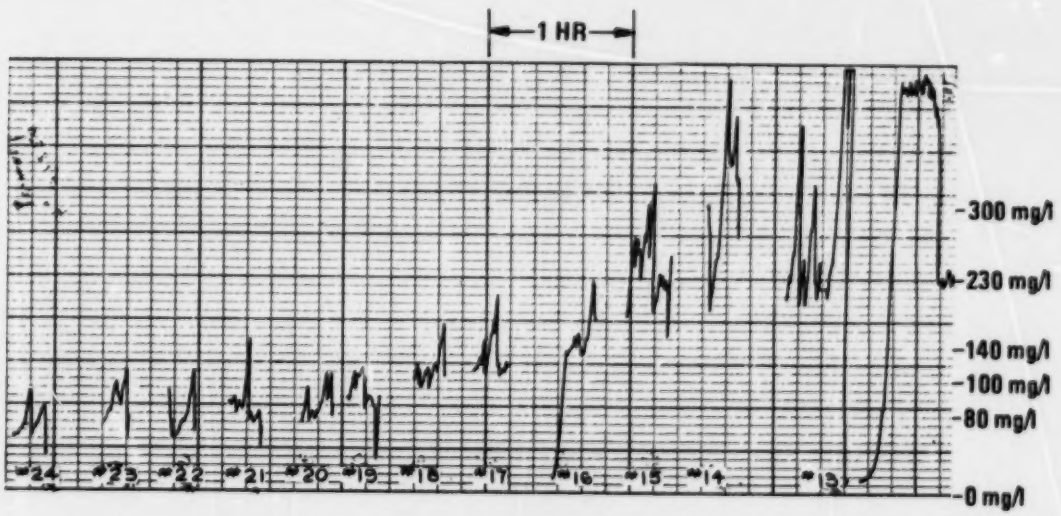


Figure 7. TOC chart for the storm of 5/10/74

Table 3. DATA FROM SAMPLES OBTAINED AT COTTAGE FARM STORAGE FACILITY, STORM OF 4/23/74

Characterization		Sample Number										
		1	2	3	4	5	6	7	8	9	10	11
Suspended Solids mg/l		205	156	169	141	121	103	104	101	103	82	84
Volatile Suspended Solids mg/l		112	97	110	92	86	76	71	70	71	84	62
Soluble Organic Carbon (Beckman)	1.	102	196	173	162	128	115	122	128	120	116	117
	2.	123	194	172	158	128	121	121	125	120	120	108
	3.	122	198	174	164	128	121	114	128	125	115	120
	4.	102	206	173	144	110	110	111	114	124	117	119
	5.	123	206	176	167	130	121	118	115	118	117	119
Mean	mg/l	115	200	174	159	125	119	117	122	121	116	117
Total Organic Carbon (TOC) (Beckman)	1.	185	247	214	191	188	150	128	137	140	131	132
	2.	168	243	217	195	163	140	157	140	160	150	130
	3.	198	253	230	192	167	157	150	138	153	135	120
	4.	184	245	257	194	175	165	145	131	157	141	141
	5.	180	252	210	218	156	142	155	150	153	125	130
Mean	mg/l	183	244	226	198	170	151	147	139	151	136	131
Stormwater TOC mg/l		161	238	215	202	158	150	140	142	142	149	135
Settleable Solids 30 Min.		Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace
pH Stabilized		2.0	1.9	2.2	2.3	1.9	2.1	2.1	2.0	2.0	2.3	1.7

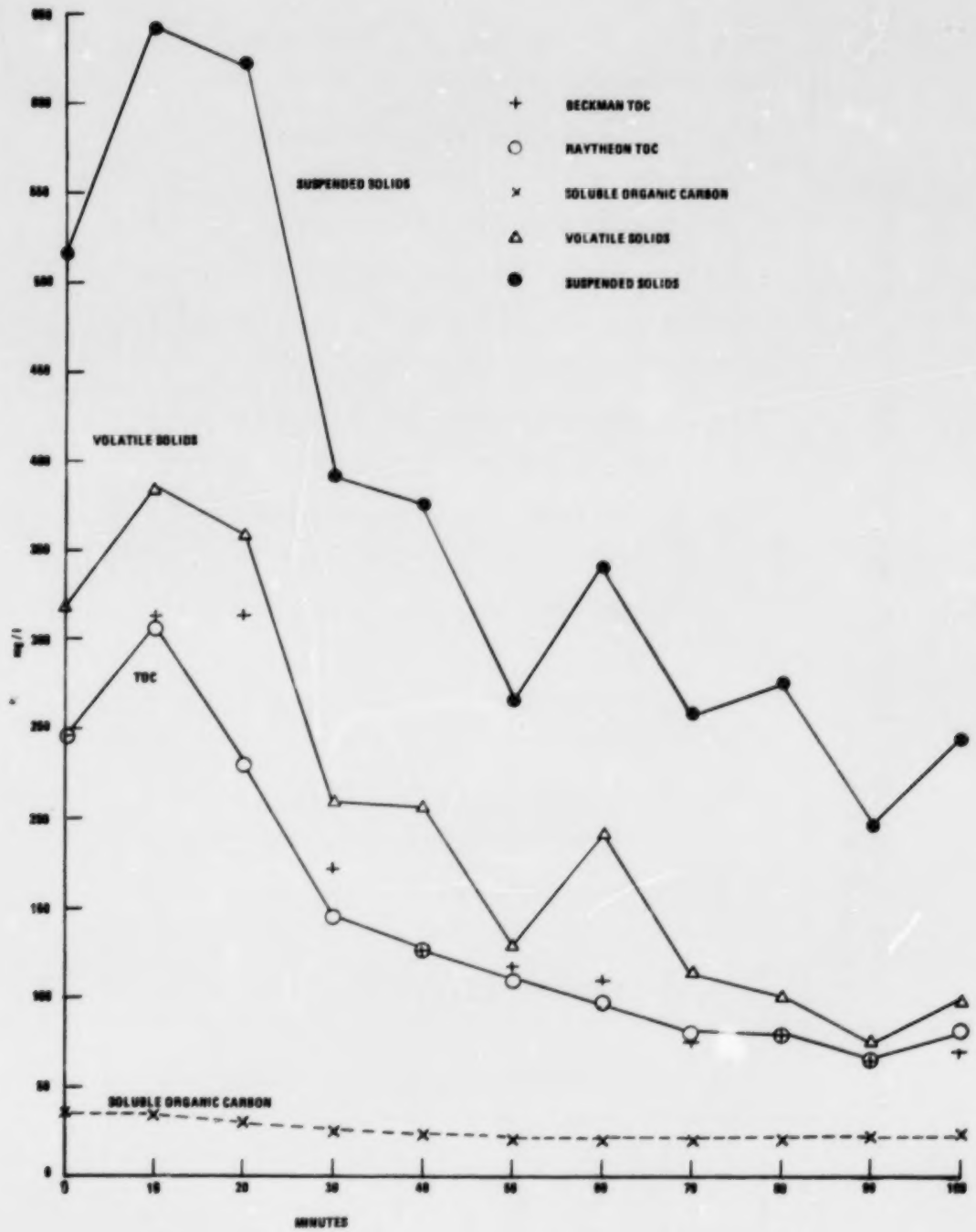


Figure 8. Characterization of the storm of 5/10/74

Table 4. DATA FROM SAMPLES OBTAINED AT COTTAGE FARM STORAGE FACILITY, STORM OF 5/10/74

Characterization	Sample Number											
	13	14	15	16	17	18	19	20	21	22	23	24
Suspended Solids mg/l	515	644	624	391	377	266	338	259	274	195	248	174
Volatile Suspended Solids mg/l	320	387	359	208	206	129	193	114	100	75	99	75
Soluble Organic Carbon (Beckman)	36	36	30	25	23	22	22	22	20	21	23	36
	37	36	30	26	23	22	17	20	23	23	23	33
	37	36	35	30	23	22	22	20	22	24	25	32
	36	36	30	25	23	22	17	22	21	23	23	37
	36	36	33	25	23	22	22	23	20	21	24	33
mg/l Mean	36	36	32	26	23	22	21	21	21	22	24	34
TOC (Beckman)	240	329	320	175	125	119	119	95	82	72	60	58
	246	287	312	168	115	124	101	76	68	67	73	63
	262	337	312	177	148	104	94	60	95	60	63	62
	228	318	312	165	129	129	112	76	72	73	82	54
	244	290	339	177	119	107	122	76	84	63	70	60
mg/l Mean X	244	312	319	172	127	116	110	77	80	67	70	59.4
Std. Dev. S	12.25	22.69	11.70	5.55	12.81	10.78	11.41	12.39	10.6	5.61	8.68	3.5
Raytheon Stormwater TOC	215	280	188	134	112	104	80	68	80	68	60	45
	243	210	240	140	120	117	94	85	76	50	68	52
	359	300	265	145	135	100	105	68	76	60	95	67
	205	395	290	135	130	110	112	72	76	60	95	67
	189	350	200	145	150	120	75	81	110	80	84	85
	255	310	212	170			85	92	65	65	98	54
	265		205					94	65			64
	215											75
mg/l Mean X	243	307	230	144	129	110	92	80	79	65	81	63
Std. Dev. S	56.47	62.91	35.13	13.20	14.55	8.44	14.52	10.94	16.56	10.49	16.61	13.97
Settleable Solids cc/100	4	5	3.5	2.5	2.0	1	Trace	Trace	Trace	Trace	Trace	Trace

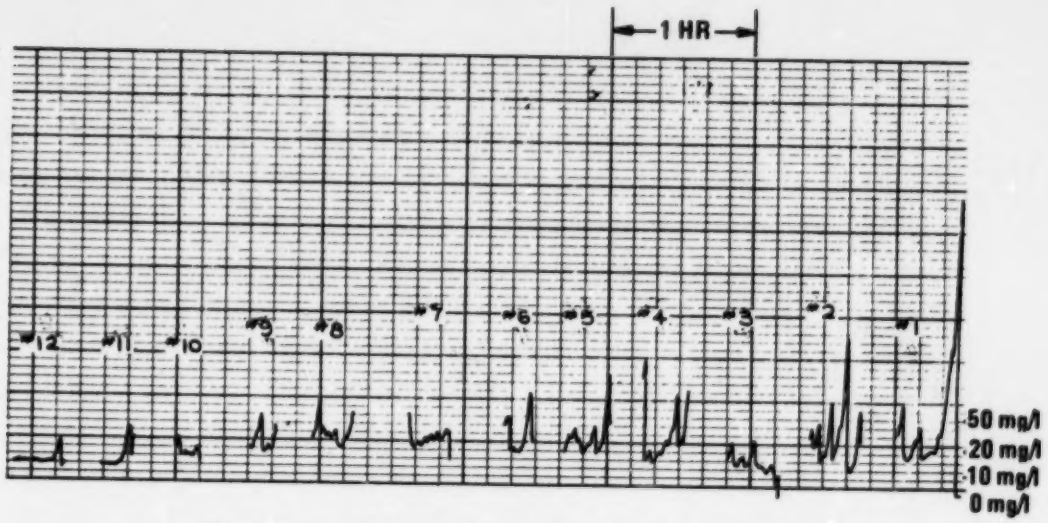


Figure 9. TOC chart for the storm of 5/12/74

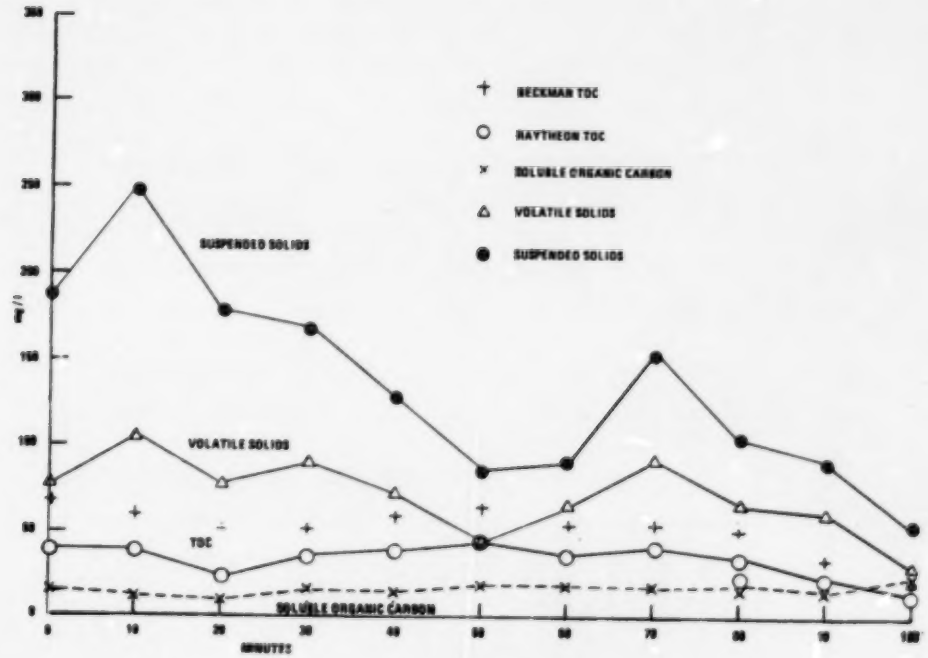


Figure 10. Characterization of the storm of 5/12/74

Table 5. DATA FROM SAMPLES OBTAINED AT COTTAGE FARM STORAGE FACILITY, STORM OF 5/12/74

Characterization	Sample Number											
	1	2	3	4	5	6	7	8	9	10	11	12
Suspended Solids mg/l	188	247	178	168	128	86	92	151	105	91	53	59
Volatile Suspended Solids mg/l	78	105	78	90	72	45	65	91	65	61	32	46
Soluble Organic Carbon (Beckman)	15	12	10	16	15	19	20	17	21	18	21	27
	15	12	10	17	15	19	20	20	21	19	27	29
	15	12	10	17	15	17	20	20	18	18	26	27
	15	17	10	18	15	19	20	19	20	19	26	26
	15	12	10	16	17	19	17	19	20	18	27	27
mg/l Mean	15	13	10	17	15	19	19	19	20	18	25	27
TOC (Beckman)	60	65	54	48	53	66	55	58	62	44	30	30
	71	44	48	50	52	55	56	60	45	43	32	33
	58	46	47	52	66	54	52	55	44	43	32	32
	76	84	50	55	57	40	51	46	75	70	33	30
	74	48	54	57	62	98	54	50	43	56	25	40
mg/l Mean X	68	57	51	52	58	65	54	54	54	51	30	33
Std. Dev. S	8.26	17.05	3.29	3.65	5.96	19.59	2.04	5.76	14.20	11.86	3.21	4.12
Raytheon Stormwater TOC	60	42	20	35	75	72	40	45	37	20	15	10
	27	35	20	37	35	50	37	37	28	20	10	10
	26	48	20	55	28	27	37	30	25	20	10	10
	42	26	23	35	35	27	38	37	53	20	10	10
	50	45	35	33	32	56	30	34	37	30	10	11
	27	30	10	27	26		33	34	30			
	30	50		20	35		36	55				
	42			35				59				
mg/l Mean X	38	39	23	39	38	46	36	41	35	22	11	10
Std. Dev. S	12.59	9.27	8.72	9.97	16.71	19.45	3.34	10.60	10.06	4.47	2.24	.45
Settleable Solids pH ≈ 2	<1cc/100											

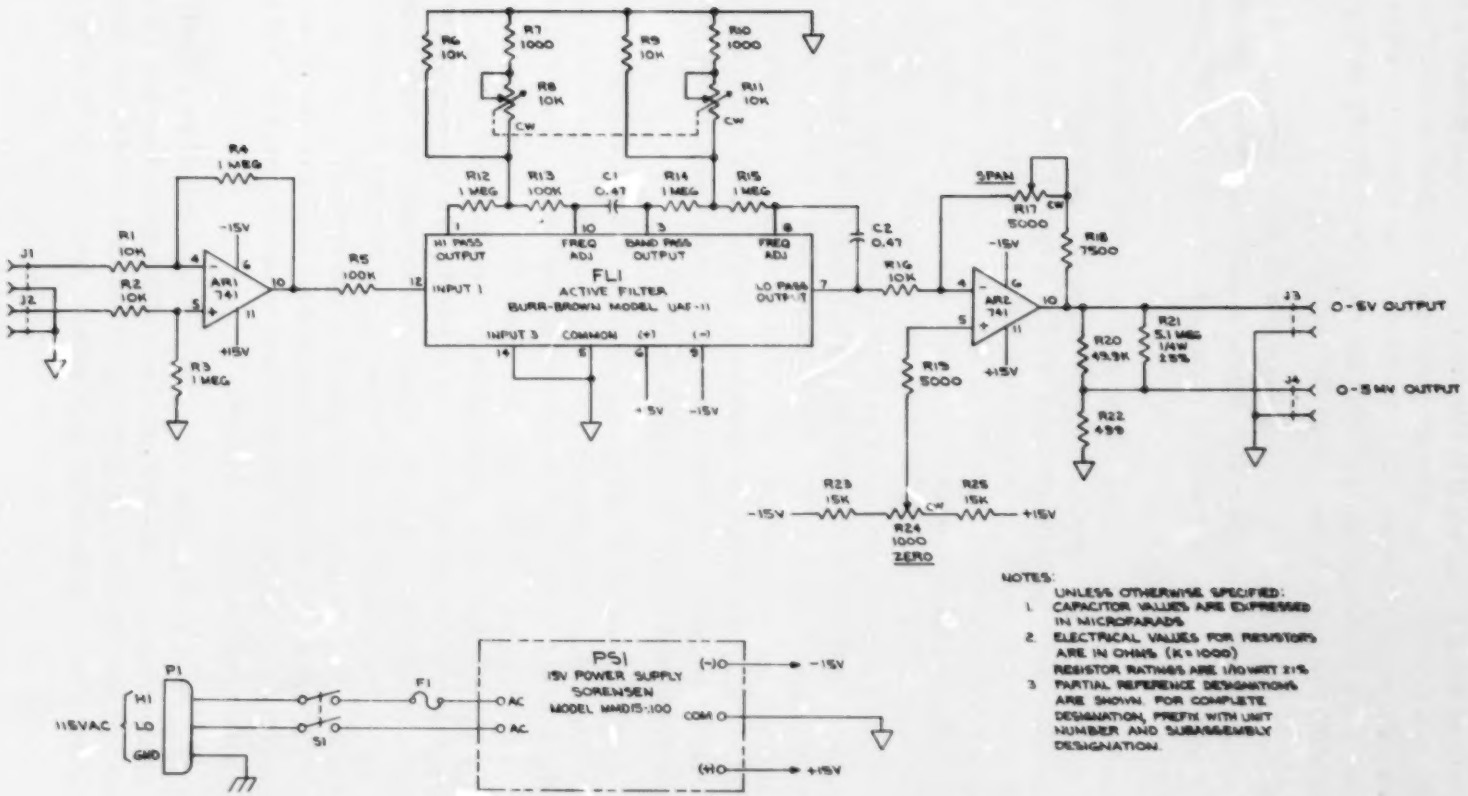
To meet the severe sample loading that the stormwater sample presents to the TOC analyzer, two modifications were explored. One of these was to improve the combustion efficiency of the reactor; the other was to modify the signal. Both techniques were investigated. Between the two alternatives, an improvement in combustion characteristics was preferred.

In order to improve the combustion characterisitcs of the reactor, two design changes were initiated; the sample delivery tube cooling jacket was insulated from the reactor body. A cooling jacket temperature control was installed in the instrument.

Another method of producing a signal representative of the stormwater TOC content is by integrating the signal either electronically, or physically in time. It would appear that this approach would be valid if it were implemented since Raytheon is displaying means and the means of the continuous analyzer tend to approach the means of the discrete Beckman samples, even though the variance might be quite large. This is particularly clear in the storm of 5/10/74 (see Figure 7 and 8, and Table 2). In early tests, an analog filter was designed as seen in Figure 11. It worked well but was more expensive than the gas mixing volume added to the outlet of the condenser. The gas mixing volume provides an integration time of four minutes. The effect of this added gas mixing on the integration time can be seen in Figure 12. This 4-minute integration time in conjunction with intensive combustion techniques produced the improved data in Figure 13. These data were collected on the storm samples from Boston on June 1 and are presented in Figure 14, 15 and 16.

Signals were developed with and without the addition of a gas mixing volume. The noise was diminished dramatically. The standard deviation of the data collected in the absence of the mixing volume had been about 12%. With the added volume, this was reduced to about 3%. This can be seen by an examination of the data in Table 6. The data obtained without the additional gas mixing volume are presented in Figure 14; they are separated for the purpose of defining the discontinuity between samples. Figure 15 presents the same samples run with the added gas mixing volume. These are presented as a continuity to better indicate how such a signal would appear in the continuum of an actual storm event. The complete characterization is seen in Figure 16. These curves show the close proximity of the Beckman means to the stormwater TOC means, both with and without added mixing volume.

In summary, the problem of suspended solids has been solved by effective homogenization, careful transport and delivery, and efficient combustion and processing techniques that lead to a uniform signal that is a quantitative measure of the stormwater TOC. Unlike other commercial devices, the developed TOC



NOTES:
UNLESS OTHERWISE SPECIFIED:
1. CAPACITOR VALUES ARE EXPRESSED IN MICROFARADS
2. ELECTRICAL VALUES FOR RESISTORS ARE IN OHMS (K=1000)
RESISTOR RATINGS ARE 1/10 WATT 2%
3. PARTIAL REFERENCE DESIGNATIONS ARE SHOWN. FOR COMPLETE DESIGNATION, PREFIX WITH UNIT NUMBER AND SUBASSEMBLY DESIGNATION.

Figure 11. Analog filter schematic

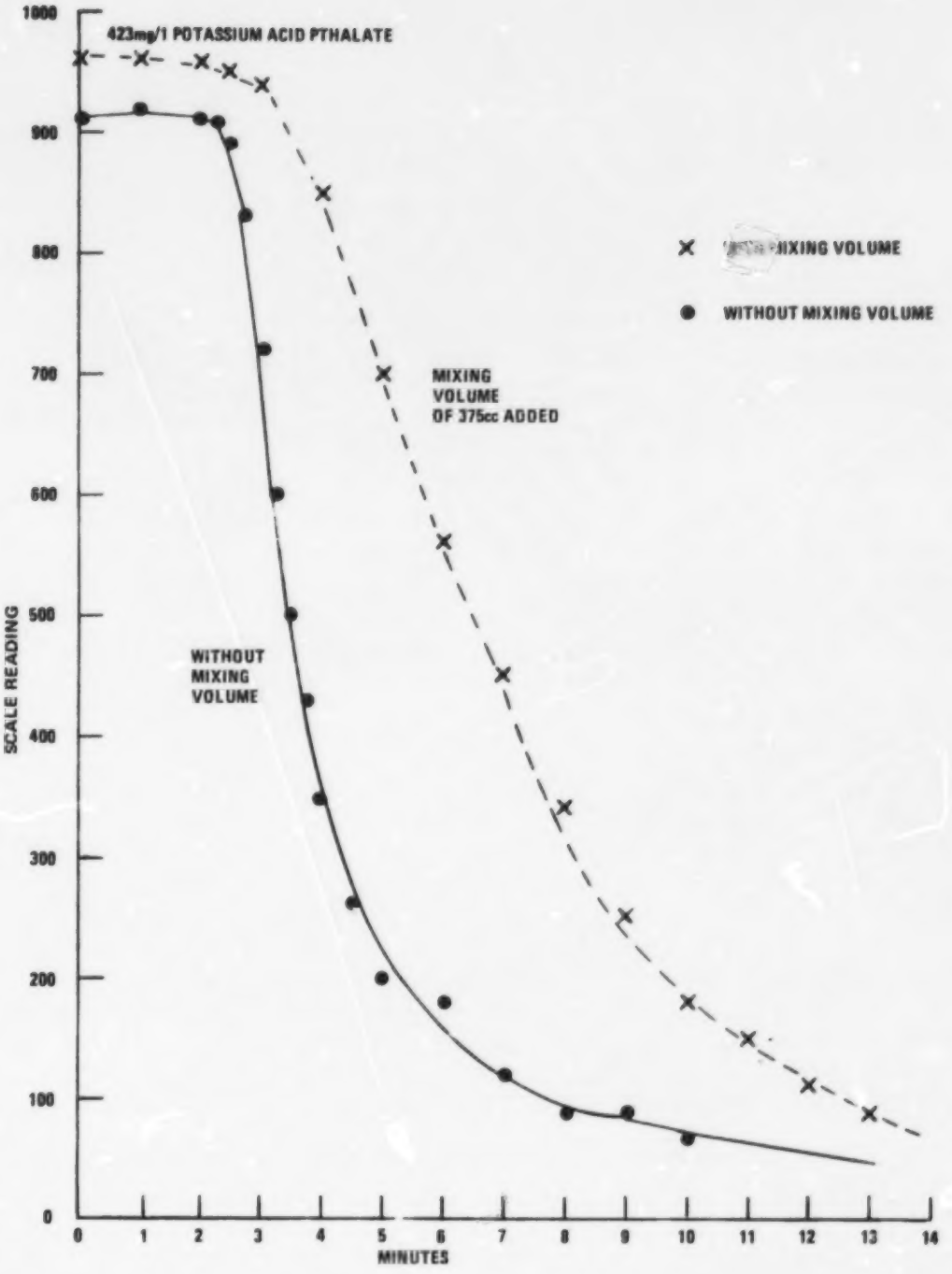


Figure 12. Integration Time Using Mixing Volume

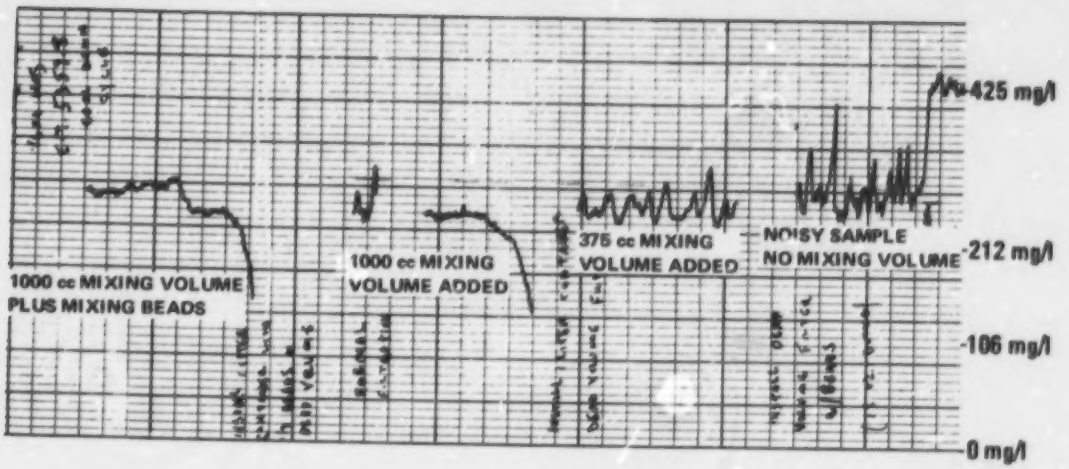


Figure 13. Effect of added mixing volume

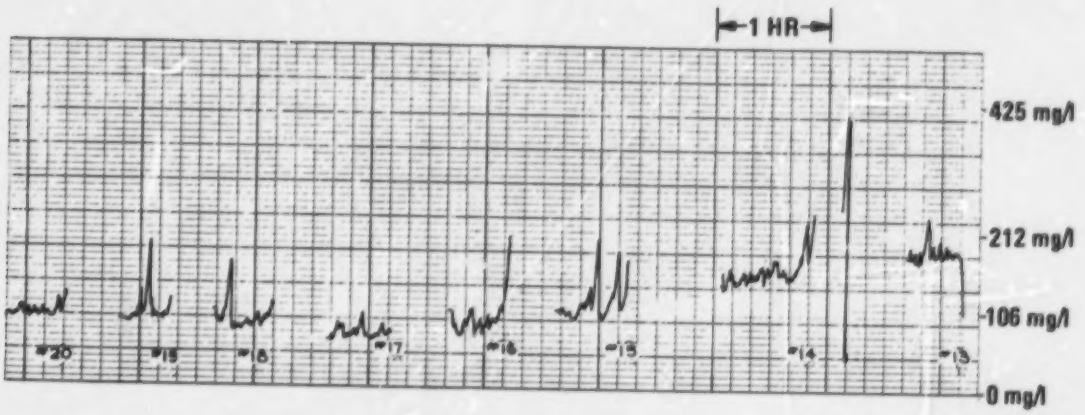


Figure 14. TOC chart for the storm of 6/1/74 without added mixing volume

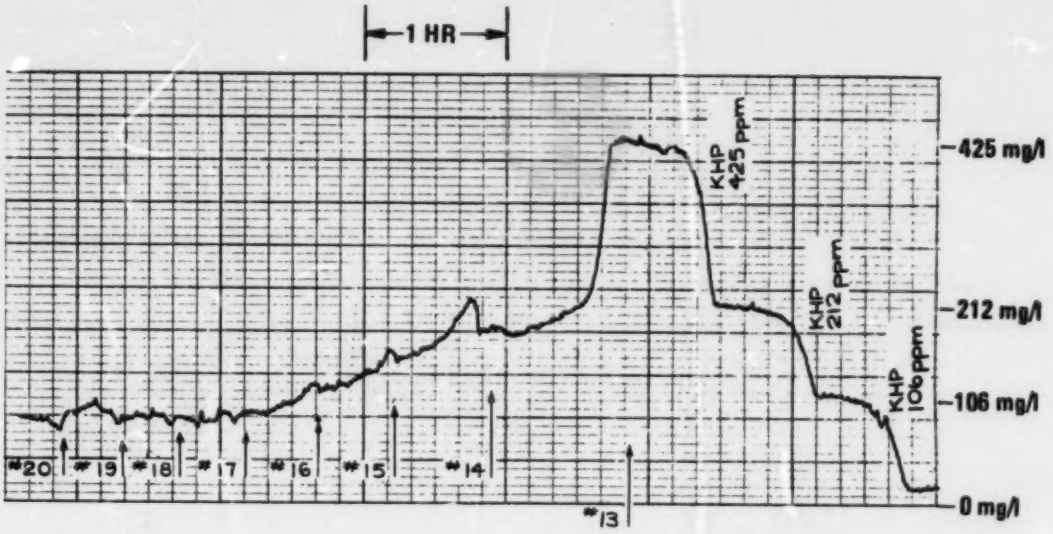


Figure 15. TOC chart for the storm of 6/1/74 with added mixing volume

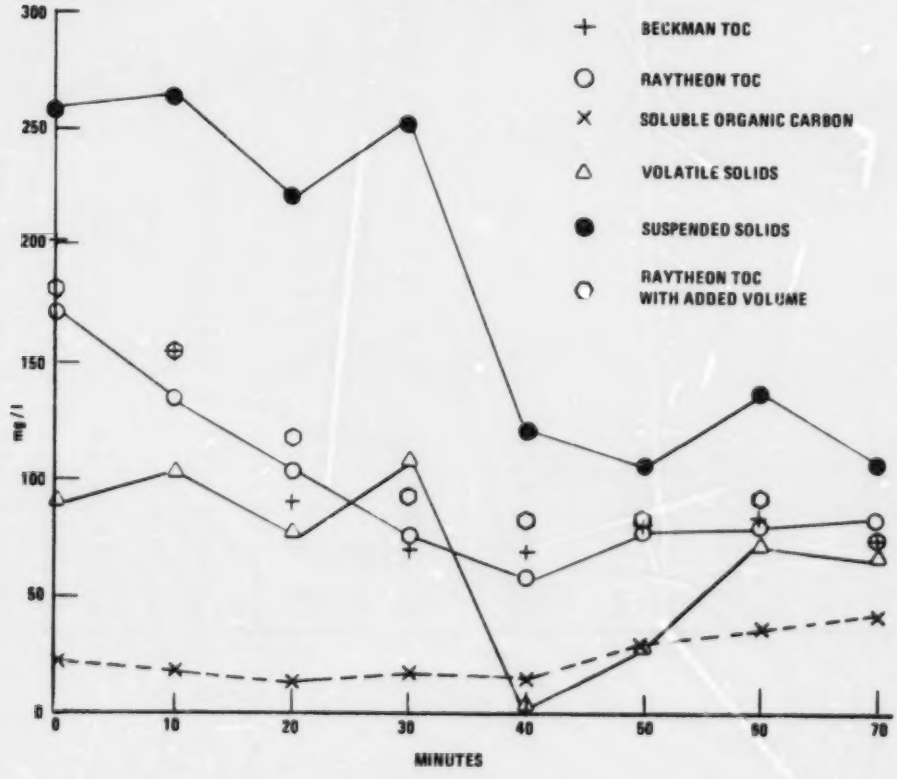


Figure 16. Characterization of the storm of 6/1/74

Table 6. DATA FROM SAMPLE OBTAINED AT COTTAGE FARM STORAGE FACILITY, STORM OF 6/1/74

Characterization	Sample Number							
	13	14	15	16	17	18	19	20
Suspended Solids mg/l	360	263	224	254	123	106	145	102
Volatile Suspended Solids mg/l	90	101	77	105	8	27	71	66
Soluble	25	21	14	15	13	28	34	39
Organic Carbon	25	19	14	14	13	28	32	38
(Beckman)	20	18	15	15	12	28	35	41
	21	17	15	15	14	25	34	38
	23	17	14	14	16	28	34	38
mg/l Mean $\bar{X}$	23	18	14	15	14	27	34	39
Std. Dev. S	2.28	1.67	0.55	0.55	1.52	1.34	1.10	1.30
TOC	176	211	115	53	86	82	107	84
(Beckman)	188	162	94	73	50	71	75	84
	212	149	70	84	73	62	73	75
	216	128	90	63	75	71	73	75
	207	119	82	75	60	80	77	64
mg/l Mean $\bar{X}$	200	154	90	70	69	73	81	76
Std. Dev. S	17.09	36.19	16.62	11.91	13.99	8.04	14.63	8.26
Raytheon Stormwater	163	163	126	91	59	75	75	87
TOC	170	140	100	75	67	79	75	91
	172	131	122	75	55	71	83	75
	183	133	117	67	55	67	83	79
	168	144	140	67	55	67	95	79
	193	140	104	87	59	63	75	75
	168	133	91	70	55	108	71	87
	193	131	79	58	59	71	71	75
	168	131	83	87	51	75		71
	153	128	87		51	83		
	172	128	87					
		131						
		128						
mg/l Mean $\bar{X}$	171	135	103	75	57	76	79	80
Std. Dev. S	11.38	9.71	20.24	11.10	4.70	12.76	8.12	6.86
Stormwater TOC	187	165	121	98	85	85	89	72
Gas Mixing Volume	181	160	116	93	80	85	98	80
	176	156	116	89	85	80	93	80
	176	150	116	89	80	85	89	80
	187	150	111	89	85	80	85	85
mg/l Mean $\bar{X}$	181	156	116	92	83	83	91	79
Std. Dev. S	5.50	6.50	3.54	3.97	2.74	2.74	4.92	4.67

system can be standardized on KHP. The technique of signal smoothing by gas mixing volume has been demonstrated on actual stormwater samples. The gas mixing volume was employed in all later testing.

MAINTENANCE

The successful operation of an on-line TOC depends upon the maintenance program and an adequate supply of spare parts necessary to replace worn or consumed components. The remote location of most stormwater monitoring sites means that the prescribed maintenance needs must be minimized. With this in mind, the stormwater TOC system was designed with a maintenance program that will make it possible to obtain long and continuous operation of the on-line TOC. This maintenance program can be minimized by providing automatic features which will permit remote operation. Among these features, auto-zero and auto-span have been provided for the Cottage Farm Storage Facility. The maintenance tasks and frequency are shown in Table 7.

Table 7. MAINTENANCE REQUIREMENTS

MONTHLY	1) Replace sample delivery veins 2) Check reactor pressure 3) Chart paper and ink supply 4) Replace span gas 5) Clean reactor well 6) Replace homogenizer gland 7) Lubricate peristaltic pump motors
TRI-MONTHLY	1) Clean Lira and replace filter 2) Renew acid supply
SPARE PARTS	1) Replacement reactor 2) Replacement sample delivery motor 3) Replacement Lira filter 4) Span gas 5) Asco solenoid 6) Replacement gland for homogenizer

In laboratory studies, Raytheon established that under present operating conditions, it is possible to substitute CO_2 free air for oxygen. The preparation of this material can be automated and would eliminate the need for periodic oxygen replacement. Since oxygen is inexpensive and readily available in suitable purity, it was used for the field demonstration program. Our maintenance experience shows that plugging by refractory solids (salts and lime) has not occurred in six months of operation. Although reactor flushing is not needed, the field demonstration model contains flushing equipment which is also used for rapid reactor cooldown.

A program providing biweekly maintenance and exercise of the instrumentation on-line at the Cottage Farm Storage Facility was instituted.

The assembly of instrumentation has operated at theCranston Municipal treatment plant for a continuous period of 5000 hours. If a storm lasts an average of 2 1/2 hours, 5000 hours can be equated with 200 storm-event equivalents. Clearly the life of the instrument in the stormwater installation will be determined by conditions other than instrument use.

The limitation on the usefulness of the stored and unpowered instrument is the vein life of the Tygon tubing in the peristaltic pumps. This material undergoes cold flow on standing and experiences wear in use. In the standby condition, use of the pumps minimizes the effect of cold flow. This can be programmed into the control circuit if necessary. The standby condition does require the continuous operation and control of heaters for the reactor as well as the infrared detector. Heaters have a limited life and would be expected to limit the life of the hardware. Another factor that might be expected to present a problem for the instrument itself is corrosion of various components in the system. This would be dependent on how the system is used, protected, ventilated, and maintained.

To get a sense of reliability of the stormwater TOC installation, a reliability estimate was made as shown in Appendix 1. In this estimate, it is determined that the mean-time-between-failures is 3,557 hours. Factors that are more likely to limit the collection of useful data during storms are likely to be: inadequate maintenance, failure of the sample delivery system to the instrumentation, or neglect of the hardware after accidental shutdown, as will occur during power failure or temporary loss of water.

SECTION VI

INSTALLATION OF A SYSTEM IN A REMOTE LOCATION

The ability of a system of instrumentation to operate in a remote location with a high degree of reliability depends upon the probabilities of failure of each essential component in the system train. In the case of a new and advanced technology requiring a cascading of subsystems, these failure probabilities can combine to be quite large and very often result in a total unreliability (50% probability of failure) of the system. It might be valuable to digress at this point to provide an example of this type of occurrence. Consider that there is an assembly of orifices transporting a liquid (typically stormwater) in which there is a 5% probability of plugging each orifice; now cascade ten such orifices in a sample transfer system and the chances are 40% that when the system is called upon to respond it will be in an unready state. This would be a nuisance in the laboratory but a serious problem for a remote monitoring system. This is what one might expect in taking representative sample of stormwater and delivering it to the reactor of an operating TOC.

A stormwater monitoring system installation must be guided by an intention to simplify the liquid transfer process, using minimum number of components. Special care is necessary at tube connectors so hangups on shoulders will not cause plugging. Complexity that would be expected from stream selection systems, flushing, and switching would have the effect of increasing the probability of failure. To obtain a dependable measurement, it is necessary to keep the assembly as simple as possible, consistent with the needs of the stormwater monitoring application.

SAMPLE DELIVERY SYSTEM

With this problem in mind, it is essential that an operating TOC of high reliability be furnished with a sample from a highly reliable sample delivery system. The operation at the Cottage Farm Storage Facility is intended to take advantage of the sample delivery system consisting of a submerged pump located below the level of flow in the entering channel, that has been installed on-site since construction of the facility. The sample can be delivered to the stormwater TOC analyzer's homogenizer at high velocity. A stream can be separated for continuous homogenization and delivery of the TOC.

Since the design of the Cottage Farm Storage Facility, new technology has been brought to bear on the design of stormwater sampling systems. Much of this has been as a result of the work of Dr. Phillip Shelley and his team at Hydrospace-Challenger. The Hydrospace-Challenger design has provided solutions for many of the problems of stormwater sample delivery and redundancy has been provided in the system. Air and water purging, possible with the Hydrospace-Challenger delivery system, are valuable features that might interface very well with the stormwater TOC system. At this time, work is still in process which will result in the optimization and testing of the Hydrospace-Challenger's current design configuration. When the current testing programs are complete, it may become appropriate to bring the sample delivery technology and stormwater TOC technology together to produce a highly reliable stormwater monitoring system.

The limitation on the usefulness of the stored and unpowered instrument is the vein life of the tygon tubing in the peristaltic pumps. This material undergoes cold flow on standing and experiences wear in use. In the standby condition, use of the pumps minimizes the effect of cold flow. Under continuous standby use, veins must be changed at approximately one-month intervals. Other practical life limitations like heater life and corrosion are considerably longer term issues.

To get a sense of reliability of the stormwater TOC installation, a reliability estimate was made as shown in Appendix 1. In this estimate, it is determined that the mean-time-between-failures is 3,557 hours. Factors that are more likely to limit the collection of useful data during storms are inadequate maintenance, failure of the sample delivery system to the instrumentation, or neglect of the hardware after accidental shutdown, as will occur during power failure or temporary loss of water.

MANHOLE OPERATION

The prospect of installing the hardware in a manhole or in a water flooding situation was kept in mind during the design and laboratory testing of the stormwater TOC monitoring system. Considerable packaging would be required to do this (see Appendix 2). Nothing in the developed TOC monitoring system rules out the possibility of lowering the unit into a manhole.

There are, however, other manhole operational configurations that would require very little modification; for example, it would not be difficult to drop a sample delivery system into a manhole in proximity to an instrument shack containing the TOC analyser and necessary water, power, and oxygen. From this manhole, a sample could be delivered which would be processed periodically or continuously for TOC.

Alternatively, a trailer might be outfitted for the measurement of TOC. The trailer could be delivered to a manhole. Power and water could be provided from a local supply or from a gasoline generator and recirculating water supply. This would require a portable sample delivery system which could be lowered into the manhole. It should not be difficult to be on-line with very short notice.

Either the shed or trailer will provide a useful system at the inconvenience of above ground installation. Both alternatives will provide useful data.

DOCUMENTATION

The documentation that is necessary to describe stormwater TOC consists of five essential parts:

- Circuit diagram (Figure 17)
- Flow diagram (Figure 18)
- Stormwater TOC control circuit (Figure 20)
- Installation diagram (Figure 22)
- Flow manifold (Figure 23)
- Design specification of stormwater TOC (Appendix 3).

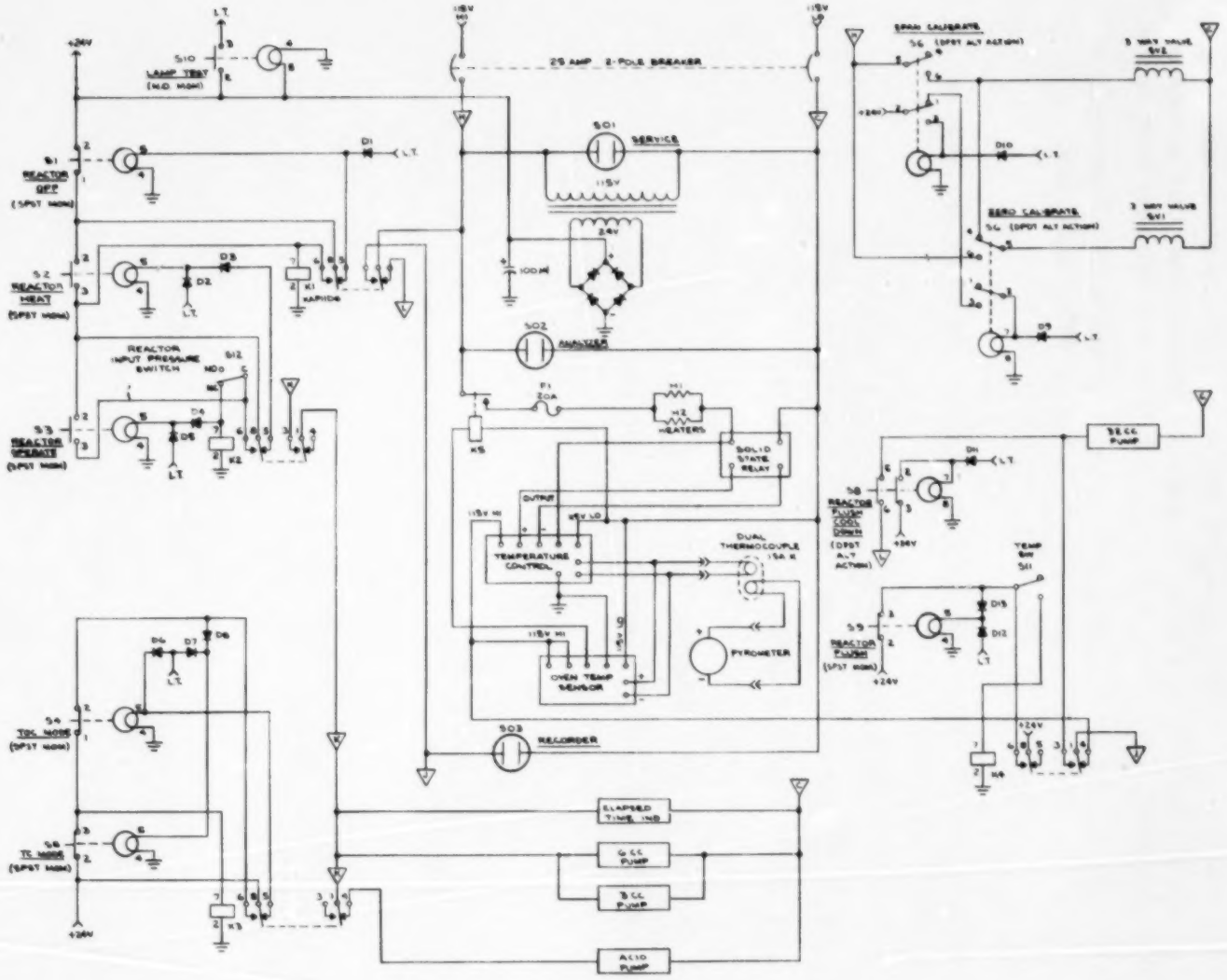


Figure 17. TOC Electrical Schematic

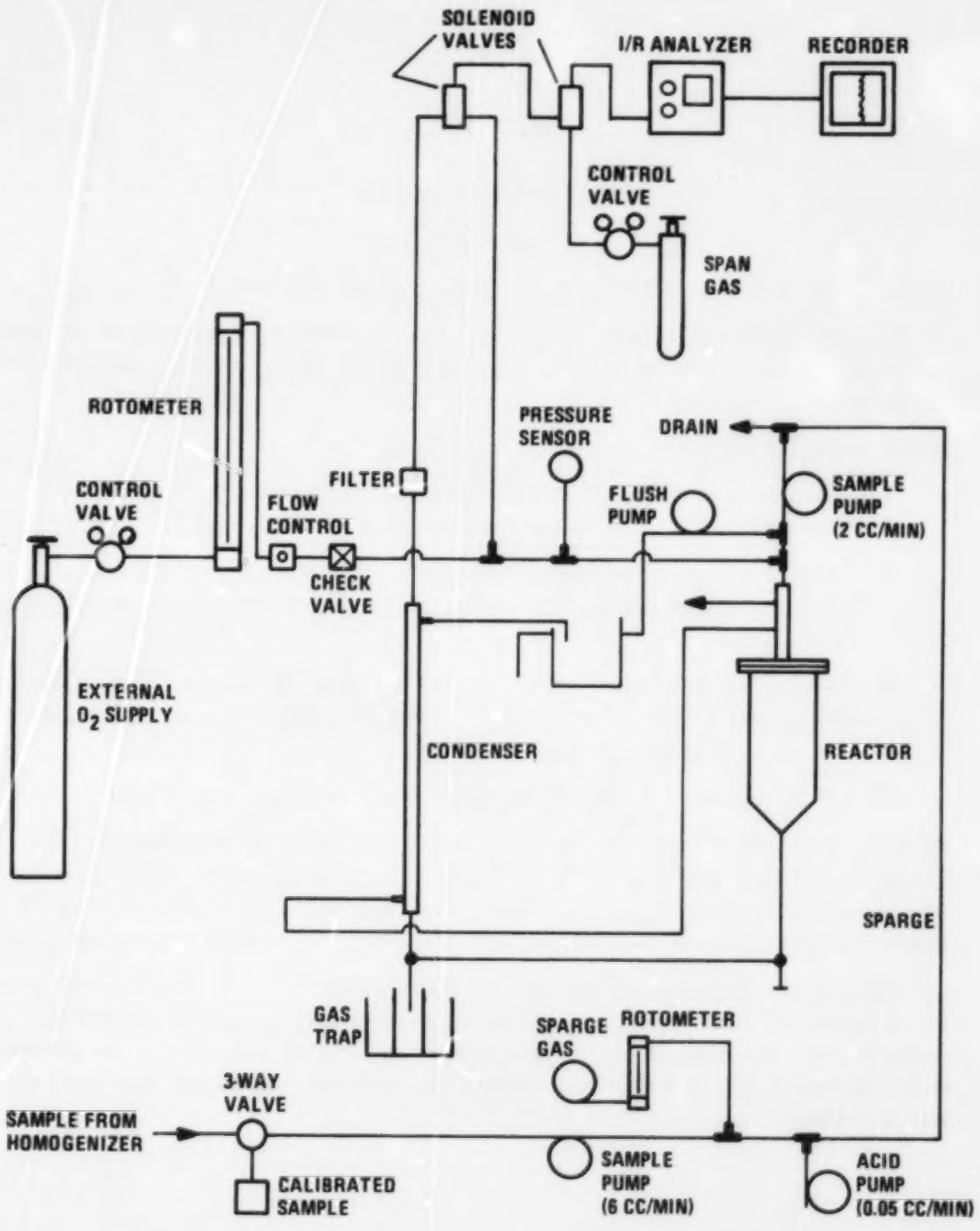


Figure 18. TOC analyzer flow diagram

SECTION VII

PHASE II—FIELD TEST

FIELD TEST INSTALLATION OF A STORMWATER TOC

On July 15, 1974, after modeling and testing a stormwater TOC system in Phase 1, the assembly was found to be satisfactory and the program was continued into Phase II.

Phase II objectives were:

1. Installation of device(s) at a suitable combined sewer site, perhaps in conjunction with an existing stormwater project, and/or
2. Installation at a sewage treatment plant influent sewer or junction overflow point where comparative analytical data could be be obtained during storm flows
3. On-site demonstration and evaluation to establish comparisons, adaptability, reliability, maintenance, and operational requirements, and accuracy under actual field conditions
4. A final report which would summarize all aspects of the program.

An automated TOC was assembled to obtain data at the Cottage Farm Storage Facility in Boston (see Figure 19). This installation was selected because the site was well maintained and provided for sample collection which could be of value in confirming and interpreting the data obtained by the instrumentation.

As stated in the design goals, it was of prime importance that the final design of the stormwater TOC hardware must be fully automated so that data could be collected with a minimum of operator attention. The Cottage Farm installation was selected to test this automated operating mode as well as the TOC design and operation.

Figure 19. Cottage Farm Storage Facility stormwater TOC installation

SECTION VIII

CONTROL SYSTEM AND ASSEMBLY

AUTOMATION AND INSTALLATION OF THE STORMWATER TOC

The stormwater TOC consists of a number of assemblies selected, modified, and designed to give the automated performance necessary for the stormwater TOC analysis (see Figure 20). The components used in this assembly are following are shown in Table 8.

Table 8. MODULAR COMPONENTS USED IN STORMWATER TOC

Component	Stormwater Modifications
Raytheon TOC	Modified for intermittent sample handling
Raytheon Homogenizer	Installed as delivered
MSA Auto-zero/Auto-span	Purchased and Installed as delivered
Turn on and Operate	Designed for stormwater application
Flush and turn off	Designed for stormwater application
Control Unit	Designed for stormwater application

In order to deliver power and provide the necessary sequencing of events, a control unit was designed which was capable of handling the turn on transient power required by the assembled hardware. All power (117 Vac, single phase, 20A) was delivered to the control box. Power was delivered through 35A rated mercury power relays to the control system operating three operational modes;

1. standby mode
2. operate mode
3. automatic flush and shutdown mode.

In the standby mode, power is delivered and controlled to the reactor heater at all times. The infrared detector is powered at all times. All other components are in the off condition until a "system on" signal is sensed.

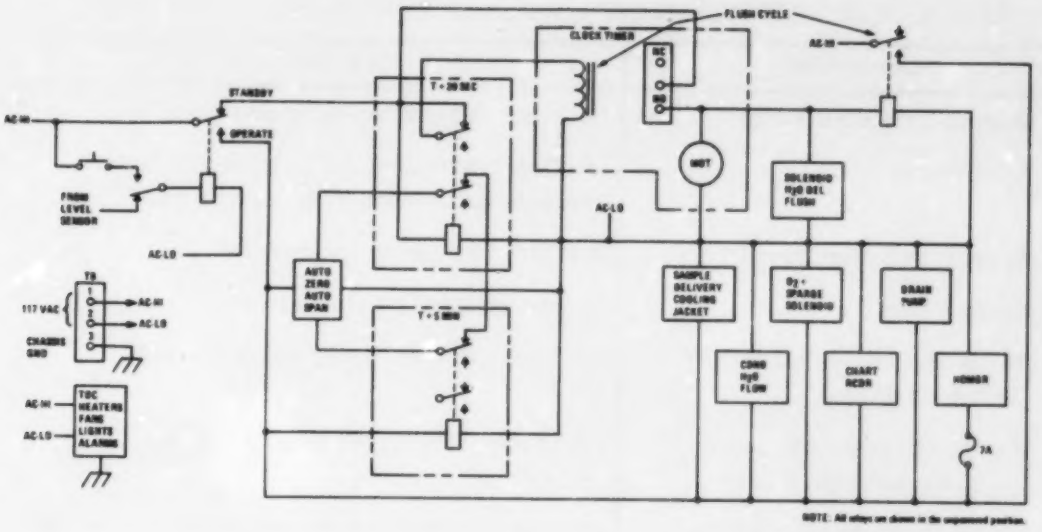


Figure 20. Stormwater TOC control circuit

In operating this instrumentation, it is desirable to obtain a sample as early as possible in the storm event. In order to do this at the Cottage Farm Storage Facility, the signal used to start up the Cottage Farm Sample Pump was also used to start the stormwater TOC instrumentation. In other operations other signals might be used. The signal needs to be early enough to activate the auto-zero and auto-span functions, and yet process the first flush loading of the storm event. This turn on signal activates all components listed in Table 9 simultaneously. The first display is the auto-zero/auto-span data which operates from the 5-minute time delay relay circuit.

Table 9. COMPONENTS ACTIVATED IN THE OPERATE CYCLE

Component	Operation
Auto-zero/Auto-span	Delivers 0_2 for automatic zero signal
	Delivers .9% CO_2 for automatic span signal
Time delay relay (t + 5 min)	Provides activation signal for auto-zero
Chart Recorder	Powers recorder for readout
Homogenizer	Begins the grinding action on the stormwater sample

Table 9. COMPONENTS ACTIVATED IN THE OPERATE CYCLE (Cont)

Component	Operation
Sample Transfer Pump	Delivers sample to the sparge system
Acid Pump	Liberates inorganic CO_2 dissolved in the sample and removed by sparge gas
Sample Delivery Pump	Delivers sample to the reactor
Drain pump	Removes water as it condenses
Normally closed condenser solenoid valve	Increases flow of water to condenser
Normally open sample cooling solenoid valve	Decreases flow of water to sample cooling jacket
Normally closed oxygen and sparge gas delivery valve	Provides oxygen for sparging and combustion

In addition to the operations described in Table 9, the 20-second time delay relay is deactivated when the start-up signal is delivered. This action completes the circuit to the flush cycle which is now ready to receive the "turn off" signal and proceed with the 1-hour flush cycle when the storm is over.

The 1-hour flush cycle acts to deliver water to the stormwater TOC sample delivery system at the input of the homogenizer (see Figure 21). The water is processed through the sample system so as to dissolve and entrain any residue that is held up during the processing of storm sample. This action prepares the instrument for the next storm.

The flush cycle is activated by a clock timer that delivers power to the operating units and signals a water delivery system that flushes the sample line and operates the unit for a period of an hour before final shutdown. The stormwater TOC system remains in this standby condition until the system command signal is again activated.

Sample Transfer and Water Flow Systems

One of the substantial problems associated with the accurate measurement of organic pollution is the problem of transferring a representative sample from an inhomogeneous flow stream. Not only do the high velocity and turbulent flow characteristics in storm or combined sewers present problems of solid segregation and non-representative sample delivery, but the entrained solids (i.e., ladders, rocks, tires, etc.) tend to tear out the sample takeoffs and associated insertions in the sewer system.

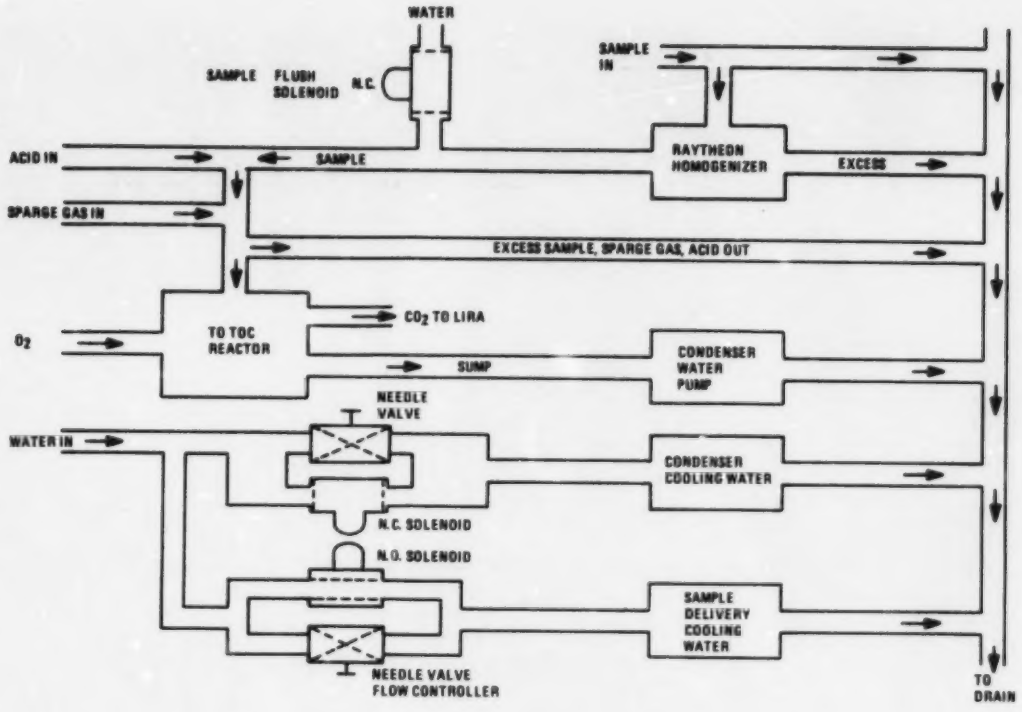


Figure 21. Manifold of the liquid flow system

There have been a number of assemblies designed to address these problems. They have been studied in Dr. Shelley's previously mentioned work. All of the commercially available sample delivery systems have been shown to have some problems associated with their operation. This was also the case at the Cottage Farm Storage Facility. Nevertheless, a sample delivery system was necessary, and there are several reasons for applying it to the measurement. The installed hardware had a basic simplicity that recommended it in the absence of available and demonstrably more reliable hardware. This simplicity of design is such as to permit repair on-site by personnel after the storm.

The sample delivery system at theCottage Farm Facility consists of a Kenco Model 93 pump rated to deliver 600 gallons per hour to a height of 60 feet. This pump is located in the flume to the wet well behind a cement support in the direct path of the flow to the wet well (see Figure 22) and beyond the bar screen of the Cottage Farm system. Even in this protected area, the pump takes severe abuse and has had a considerable repair history.

In Phase 1 simulation of storm flow, the sample delivery system in Figure 3, was assembled and found to give satisfactory quantitatively representative sample delivery. In proceeding with Phase II, it was intended that the simulated

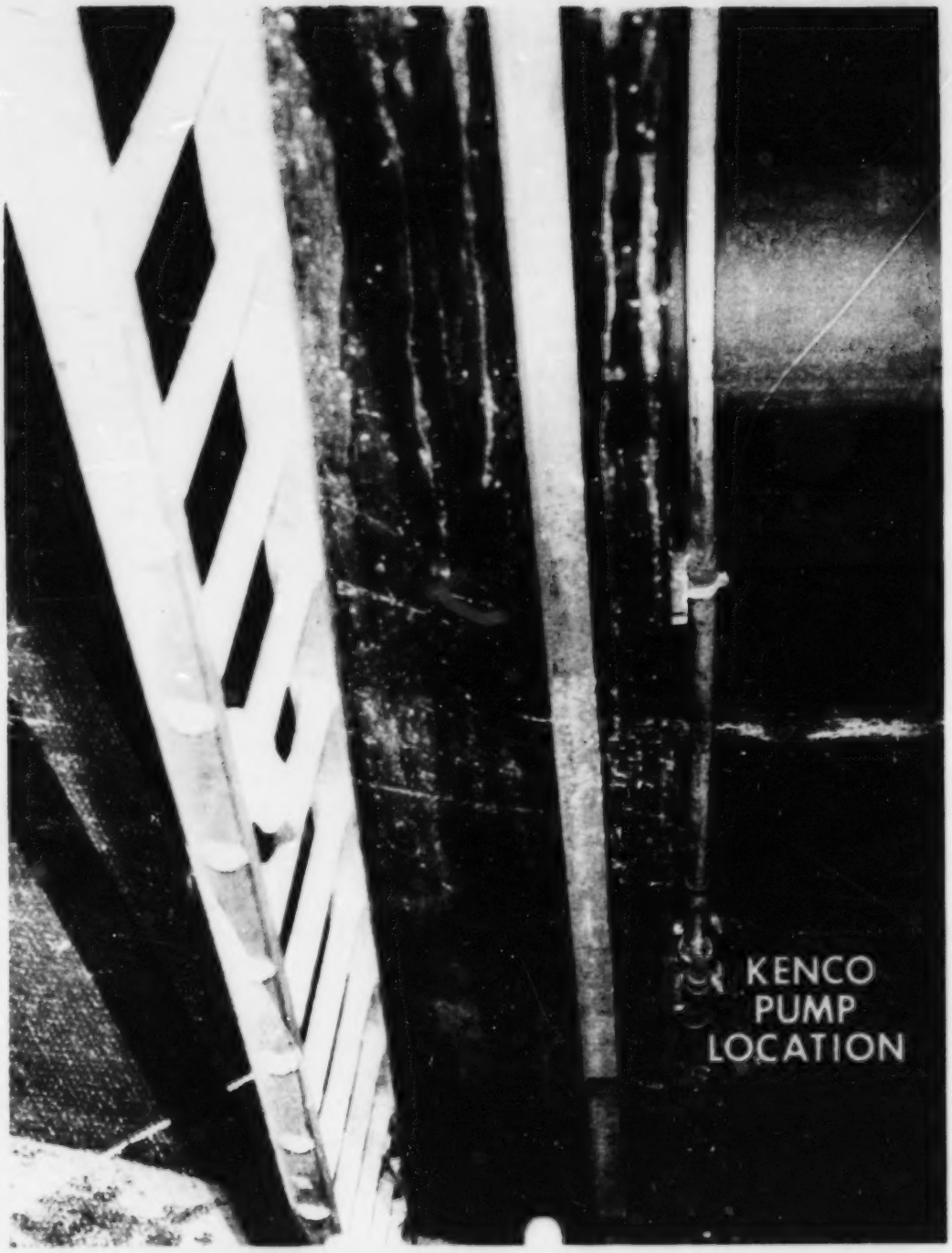


Figure 22. Location of sample take-off pump

system be followed as clasely as possible. Since the Cottage Farm Facility sample delivery system is of primary use in providing sample for the Protech sample collection unit, representative samples from this delivery system were used to compare the stormwater TOC data with the characterized discrete sample from the Protech unit (see Figure 23).

Sample, Water, and Waste Manifold

To transfer and control stormwater, cooling water, and waste in the automated stormwater TOC installation, a manifold and flow control system was devised which is uniquely applicable to standby TOC instrumentation. During standby, it is desirable that a minimum of water flow be provided for the condenser and a larger flow of water be provided to cool the sample delivery tube, minimizing the risk of corrosion and erosion at higher temperatures. The flow manifold describing the liquid flow and drain system is diagrammed in Figure 23. A photograph showing the drain and delivery assembly is shown in Figure 24. The diagram in Figure 21 shows the flow pattern for all liquids in the stormwater TOC with the solenoids in their normal, unactivated condition during the standby operation. In the operate cycle, the deactivated solenoids in the cooling water flow are actuated. The normally closed valve in the sample line is actuated to deliver cleaning water during the flush cycle.

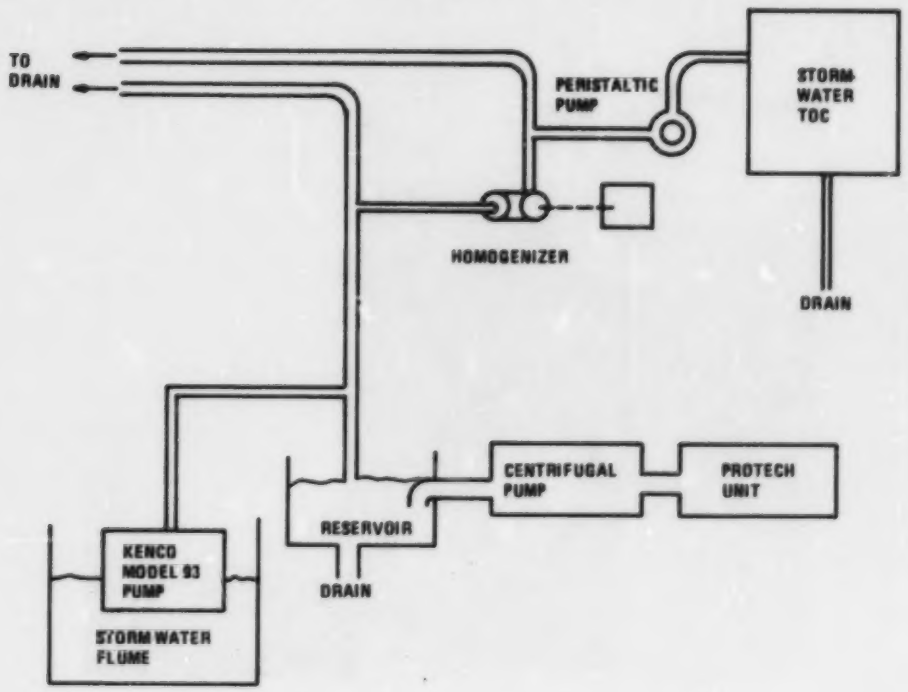


Figure 23. Installation of stormwater TOC in the Cottage Farm Storage Facility delivery system

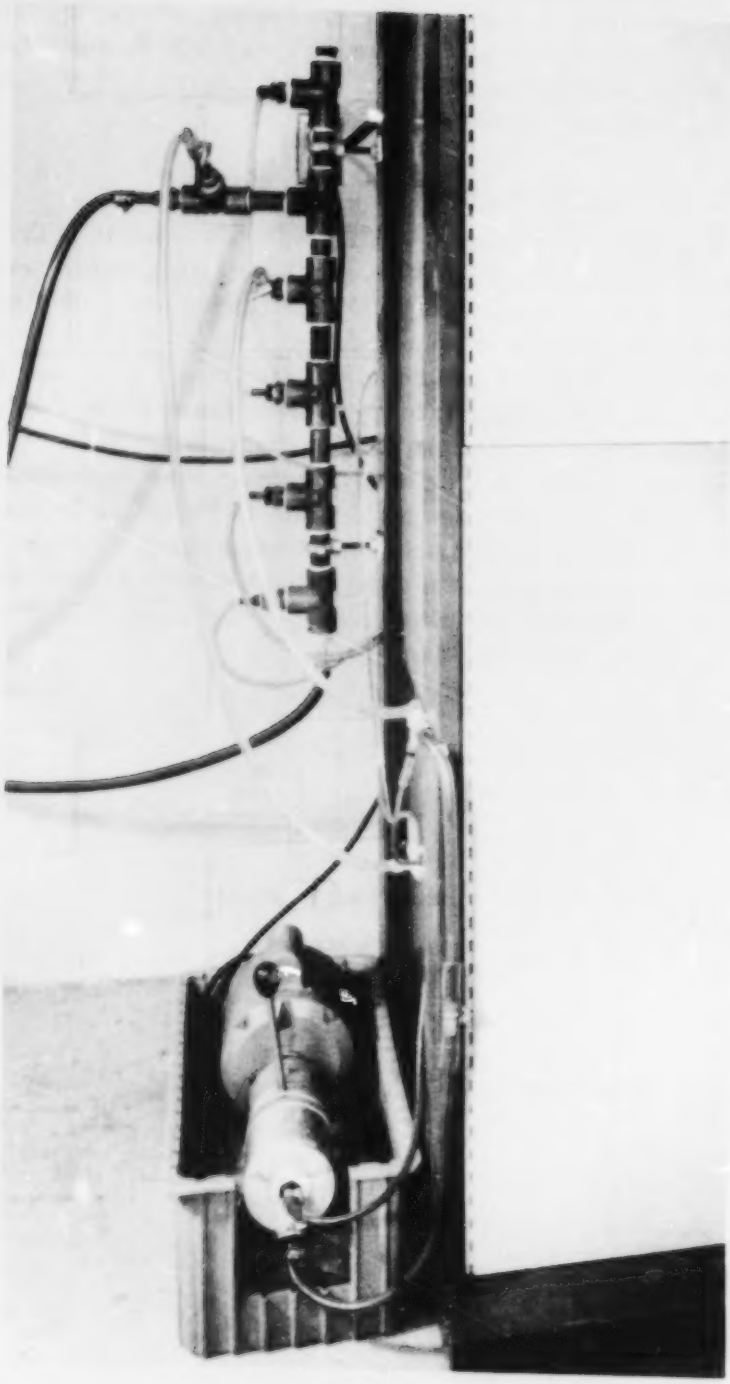


Figure 24. Sample, water, drain, and waste delivery system

SECTION IX

OPERATING EXPERIENCE

INSTALLATION, MODIFICATION, AND MAINTENANCE

After design of the assembly described in the previous section, the instrumentation was delivered to the Cottage Farm Storage Facility. The final installation was completed by October 1, 1974, after which it was found that the reliability of the Cottage Farm Facility sample delivery system was a limitation on our ability to collect data reliably. This was not surprising in view of the state-of-the-art of reliable sample delivery.

The stormwater TOC experienced one hardware failure in which the sparge pump developed bearing failure. As a result of this event, sample was not delivered during the storm of October 31. Because of this occurrence, the pump was removed from the system and sparging accomplished from the oxygen supply. This modification represented a considerable improvement in expected reliability without serious sacrifice in cost for expendable oxygen.

In order to maintain the instrumentation the program of maintenance in Table 7 (Section 4) was instituted, eliminating the need for daily zero and span adjustment. In addition, exercise of the system was provided once every two weeks. During this period, the system was calibrated. Gas supplies were checked, and the sample and signal delivery system were tested to establish proper operation of the equipment. It was not found necessary to replace either the sample delivery veins or the homogenizer glands during the intermittent operation at the Cottage Farm Storage Facility, which spanned a ten-week period.

DATA COLLECTION

The stormwater TOC instrumentation was on-line at Cottage Farm from October 1, 1974 to December 10, 1974. The first operation of the Stormwater TOC assembly took place on October 16, 1974. The data collected during that event are reported in Figure 25. On this occasion, the instrument was turned on manually some time late in the storm so that the operation of the hardware could be viewed in the presence of the skilled technician responsible for its

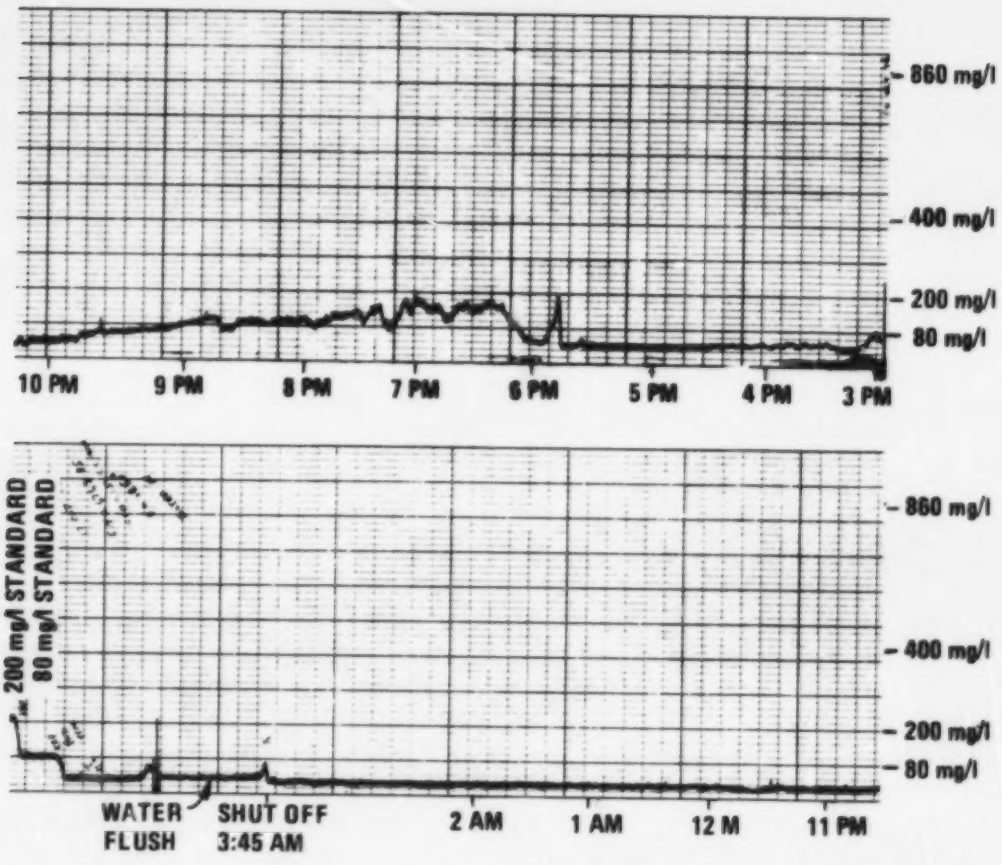


Figure 25. Operation of the Cottage Farm Storage Facility, 10/16/74

installation and maintenance. The severity and duration of the storm flow of October 16 was unusual. During this event, a considerable amount of rock and debris was entrained in the sample which resulted in damage to the Cottage Farm Storage Facility sample delivery system requiring replacement of the sample delivery pump.

The damage to the Cottage Farm Storage Facility delivery system required repair and replacement of several system components among them was the sample pump. These changes required turn on and turn off operations which activated our system in the absence of a storm repeatedly and without sample being present. This resulted in a number of unexpected and unreported start-ups at the time. During this activity, the bearing seized on the sparge pump and the span gas was depleted. Rules for reporting operation was associated with the occurrence of storm events. The problem was not recognized until a demonstration was attempted on 10/30/74 and could not be repaired in time for the storm of 10/31/74.

The next storm occurred for a half-hour during the evening of November 19, 1974. During this storm, the Raytheon instrumentation came on-line as expected. Automated features operated as designed. Data were collected as shown in Figure 26. In this figure a standardization curve is shown in which standard solutions

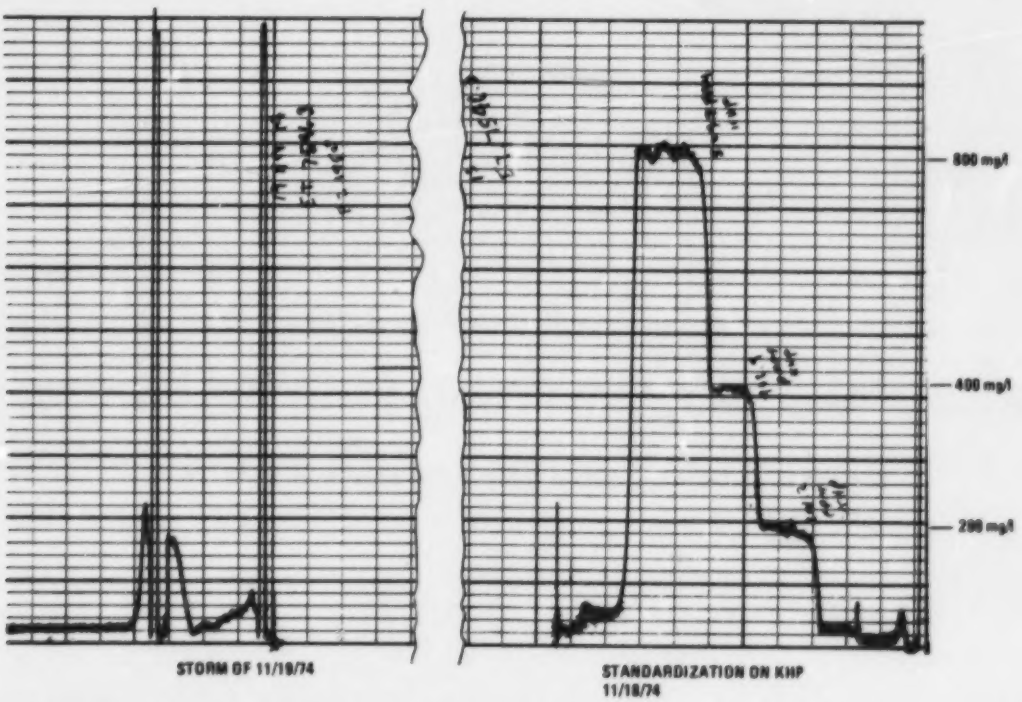


Figure 26. Display of storm data of 11/19/74 for comparison with previous day's calibration curve

of potassium acid phthalate, KHP, were passed through the TOC unit. Here we see the uniform combustion characteristics that are obtained with this standardization. This procedure scales the unit at three points, 201 mg/l TOC, 402 mg/l TOC, and 804 mg/l TOC.

On December 2, 1974, a very severe storm hit the Cottage Farm Storage Facility (see Figure 27). The system turned on and operated in its automatic mode for a period of about 15 minutes. At that point in time, sample delivery to the stormwater TOC failed. The signal that is used to start up the pumping station is also used to start the TOC analyzer. The frequent number of zero and span signals indicate that the pump had several starts and stops during the storm of December 2. The operation of the instrumentation was described to the contractor by the Cottage Farm Storage Facility plant manager; at that time, a storm was occurring and the instrumentation was reading zero. The contractor's technician arrived during the storm and reported that a pump failure had occurred. The stormwater TOC unit was standardized to verify that it was operating and that it could have processed a storm if sample had been delivered. When the operator of the Cottage Farm Storage Facility realized that the pump was not functioning, he shut off pump power, which in turn, shut off the stormwater TOC system. This was the last operation of the stormwater TOC system during storms at Boston's Cottage Farm Storage Facility.

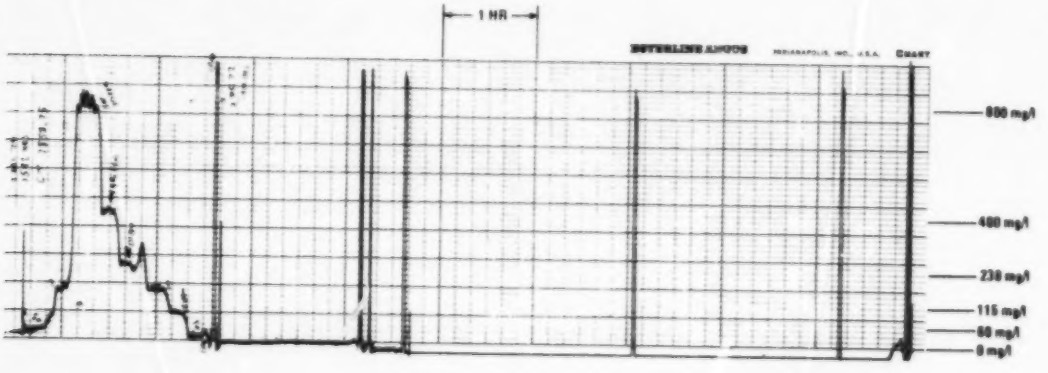


Figure 27. Data collected during the storm of 12/2/74

The data collected on the unit during the test period are encouraging. The reliability of the measurement in this particular test was largely limited by the ability of the sample transferring system to deliver a sample continuously during the severe conditions that were associated with storm flows.

Several successful experiences in data retrieved suggest that this stormwater TOC could be used as a permanent feature in a stormwater center such as that at the Cottage Farm Storage Facility.

SECTION X

APPENDICES

APPENDIX 1

RELIABILITY

The failure rate of instrumentation when plotted against time tends to follow the typical bathtub curve in which failure, at first, may occur with some high probability determined in large part by assembly errors or component failures associated with manufacturing quality control. Problems of this type are corrected by repair and replacement as necessary. When these initial problems are corrected, the instrumentation enters a period in which the reliability can be assessed by referencing the failure rate of the individual components. In the course of continued operation, wear, sooner or later, becomes a problem. Failure rate increases because of wear and decay of various kinds. This completes the bathtub curve (Figure 28).

The initial failure modes are generally covered under manufacturers' guarantees and respond to improved quality control and engineering. The final failures caused by wear and corrosion cannot be assessed until more experience is obtained with the hardware operating as an assembly.

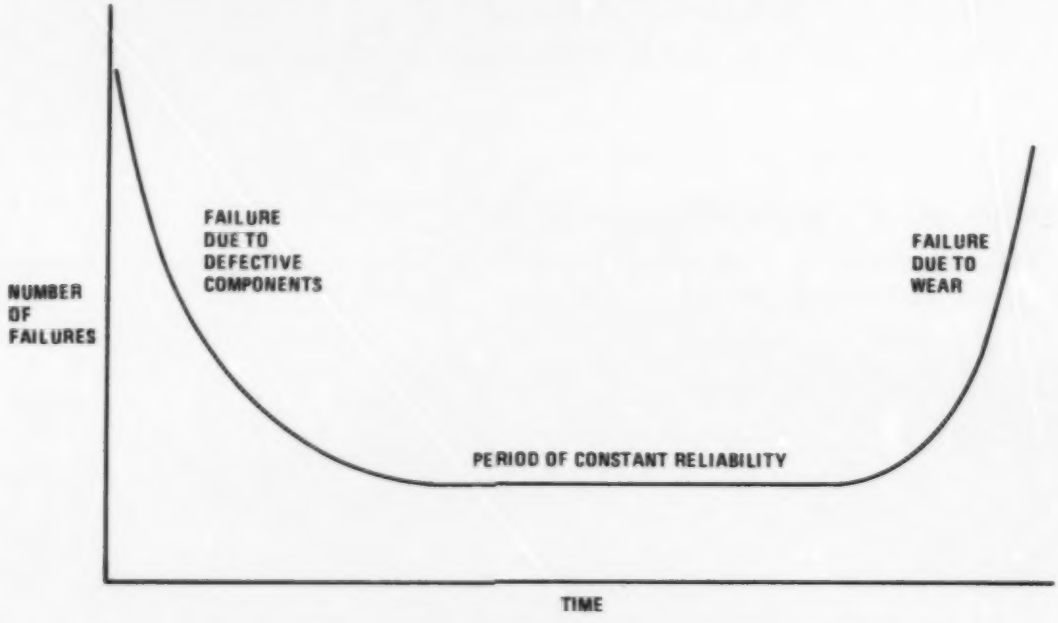


Figure 28. The bathub curve

The contractor has addressed the reliability during the interval period of constant failure rate. Data for this evaluation was obtained placing the operating components of the stormwater TOC in sequence and summing the failure rates of these individual components so as to obtain an estimate of the mean-time-between-failures (see Figure 29).

Failure rates were derived from the following sources:

1. Electrical Components (Switches, Relays, Diodes, etc.)—Failure rates have been taken from MIL-HDBK-217B and the RADC Reliability Notebook, Volume II, assuming commercial grade components and ground-fixed environment

2. Mechanical Components (Pumps, Valves, etc.)—Failure rates have been taken from AVCO Reliability Engineering Data Series. Failure rates used are the mean generic failure rates. Wearout rates are not included

3. Recorder and Analyzer Assemblies—Failure rates for the recorder and analyzer are estimates based upon assemblies of similar complexity.

The mean-time-between-failures of the assembled stormwater TOC instrumentation was calculated to be 3,558 hours.

The model and individual failure rates of the components are described in Figure 29. The sum of the individual failure rates result in an estimate of 281 failures/million hours = λ.

$$\frac{1}{\lambda} = 3,558 \text{ hours} = \text{mean-time-between-failures}$$

The reliability, R, is a probability funtion varying between zero and one in which

$$R = (1-P) = e^{-\lambda t}$$

where "p" is the probability of failure, and "λ" is the failure rate.

These data indicate a mean-time-between-failures of approximately five months for the final stormwater TOC assembly.

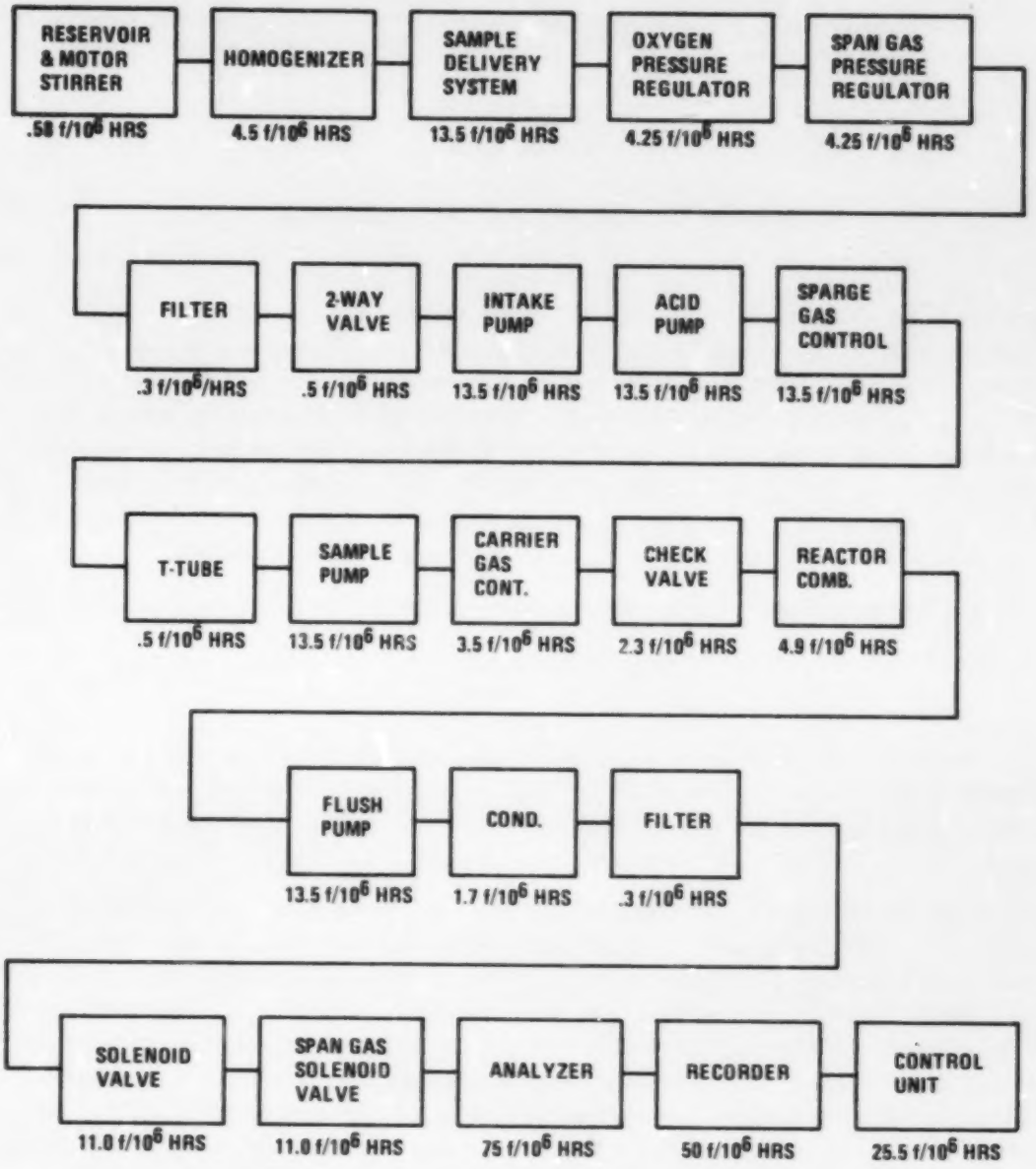


Figure 29. Reliability model for stormwater TOC analyzer

APPENDIX 2

MANHOLE MOUNTED CONFIGURATION

As has been mentioned in the body of the report, the installation of the TOC instrumentation in a manhole would require considerable engineering design. This design might well be approached by selecting hardware and assembling it in a way that will accomplish the operations detailed in Figure 1 by means of a modular design (Figure 30). The purpose of this assembly mode is to separate and isolate the operational components into discrete functional units so that failure in one of the components will not transmit its destructive effect beyond its own module. For this purpose, three modules have been chosen:

1. a pumping and sample preparation module
2. a reactor and condenser module
3. an electronic module.

This whole assembly is sized so as to be encased in a corrosion resistant steel envelope that can be sealed at the top by a compressed gasket that will protect the expensive equipment from corrosion and provide a suitable port for utilities to be delivered and heat to be removed.

If a modular design was not used, a failure in one component could do extensive damage to other components. Consider two fairly probable failures; worn pump veins and a corroded or faulty reactor. Both of these components might fail because of wear or corrosion. In a non-modular assembly, a broken pump would cause flooding of the total assembly and confine the flood so as to eventually get liquid and/or vapor to the expensive electronics and the reactor. The general effect would be to destroy the equipment totally. If the reactor should fail, the confined space of a module would allow this event to be sensed early in the storm and shut the total sample delivery and operation down.

Routine maintenance will still be necessary on this instrumentation. Because of the added complexity and exposure of the manhole-operated equipment, the mean-time-between-failures would be less than the 3,558 hours in our present assembly.

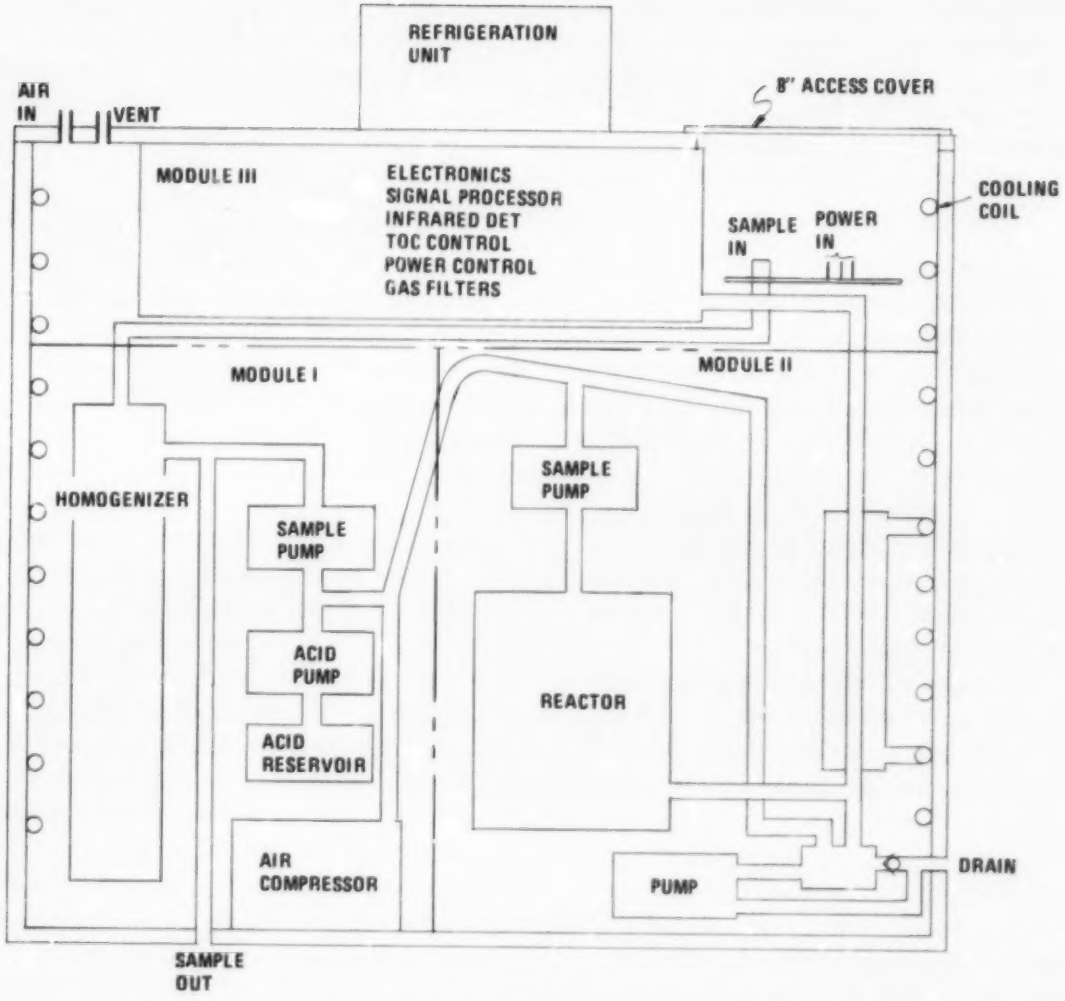


Figure 30. Modular manhole configuration

In our present assembly, the probability of failure in one month is 17%; the probability of failure in two months is 27%. This is large enough so that service should be provided at least once every two months, and would require removing the hardware from the envelope and repairing it, or replacing it with an inspected and tested assembly. This presents the problems of introduction and connection of utilities. The reliability model, which was used to describe the above-ground instrumentation, assumes that routine maintenance is provided the hardware. Raytheon has provided this maintenance once a week, and more recently once every two weeks without serious problems, but it is doubtful that this could be extended longer than once a month. It can be concluded that a design goal to improve MTBF of the manhole equipment by an order of magnitude over the above ground configuration should be established.

Some redesign will be necessary in the manhole configuration. The components must be sized so as to be able to be inserted into a manhole with a diameter of 3 feet. This requires that all components greater than that size have to be oriented so as to fit the confined space. This will require redesign of the motor bearings in order that they can be loaded vertically instead of horizontally as is the case with the present blender configuration. In an effort to confine the heat to the inside of the reactor, the reactor should be redesigned with heat being provided internally to a ceramic shell. This would have the effect of maximizing the thermal gradient at the outside of the reactor allowing for a minimum heating of air with external heaters. Alternatively, inductive heating might be adapted to this configuration. It would be much more expensive, but would provide the necessary energy only when needed. In most cases, this would not exceed three or four hours, but it would have to be sized so as to operate for the possibility of a long and extended storm. In any case, provision would have to be made for removal of the excess heat by cooling. This need for cooling would be less during standby and would have to be increased when heat is transferred during operation. A closed Freon system could be used for all cooling needs, including the condenser. This would simplify the design and eliminate the need for water in the system. Flushing of the sample delivery line would be provided externally. This has already been designed into sample delivery systems, such as that of Hydrospace-Challenger. These redesigns are difficult to say the least, and in the case of the reactor, the new design would test the state-of-the-art in this application. They are required because of the necessary total enclosure of the application. A trailer or permanent structure above ground would not require this redesign because it could be vented to the ambient atmosphere and drained with the aid of gravity. These conditions minimize the possibility of the destruction of one component by the neglected failure of another.

Freezing would not be a problem in the environment of a heated instrument in a manhole; overheating is a problem. The three possibilities for removing heat from the system are: by transfer of heat to the ambient sewage, the ambient atmosphere at the surface of the manhole or externally delivered water. Sewage would foul the heat exchanger surfaces. In certain localities, air might be provided through the manhole cover itself, but this might fail during freezing periods in the winter. Water is, by far, the most reliable heat exchanger for the purpose and might be provided externally to the instrumentation.

APPENDIX 3

DESIGN SPECIFICATION ON STORMWATER TOC

I. GENERAL

A. This specification applies to the design of a total organic carbon monitoring system to operate intermittently and on signal to measure the TOC of a sample of stormwater.

B. Applications

1. Natural streams and rivers

2. Storm and combined wastewater treatment plants and delivery systems.

C. The stormwater TOC system consists of essentially three interconnected components. One of these is a Raytheon Homogenizer used in sample grinding and delivery. The second is the singly enclosed and modified stormwater TOC unit. The third component is the MSA auto-zero, auto-span unit. The single enclosure will have front access sufficient to accomplish all calibration and routine maintenance. All required services, power, and signal connections will be made at the rear of the unit.

D. The standard output signal will be an analog voltage, 0 — 5 volts. A local meter display on the front panel will read directly in milligrams of carbon per liter of sample.

E. A local strip chart recorder will be provided to deliver continuous and permanent record of data as it is collected in time. A chart speed of 1-1/2 inches per hour will be used.

II. MEASUREMENT TECHNIQUE

A. Basic Approach

The stormwater TOC analyzer measures organic carbon content of a sample stream by mechanizing the following steps:

1. Automatically turning on all hardware from the standby mode on command.
2. Automatically zeroing and spanning the system.
3. Grinding the delivered stormwater sample containing particles no larger than 1/4 inch.
4. Removing inorganic carbon from the sample.
5. Volatilizing of the sample.
6. Completely combusting the volatilized organics.
7. Removing water vapor from the gas stream.
8. Measuring CO_2 concentration in the gas stream as an index of the organic carbon concentration in the original sample.

B. Automated features will be implemented by using the control system in Figures 20 and 23.

C. Grinding will be accomplished using a continuous motor-driven stone grinder.

D. Inorganic Carbon Removal

The sample stream is drawn from the sample line by the intake pump. Sulfuric acid is added to the stream from an internal supply container by the acid pump, converting the inorganic carbonates to CO_2 gas. Oxygen is then deliverd into the sample stream. This vigorous flow serves the dual purpose of transporting the liquid sample rapidly up to the sample pump, and stripping the CO_2 from the liquid phase. CO_2, O_2 and excess sample are led off to drain at this point. This technique for CO_2 removal is known as sparging.

E. Sample Volatization and Combustion

The sample pump, delivers a metered flow of sample from the sparging stream for delivery to the input tube of the combustion reactor. A precisely metered and controlled flow of oxygen is delivered to this point.

The multifinned, fixed-bed, noncatalytic reactor and its related heater system is required to deliver large amounts of energy on a rapid and continuous basis, and with relatively uniform distribution. On entering

the reactor, the sample vaporizes rapidly, and the volatilized organics are mixed with the oxygen so that complete combustion takes place. the end products of this process are water vapor, CO_2, and a large amount of excess oxygen, which exit the reactor as a gas stream under pressure.

F. Water Vapor Removal

The gas stream is then passed through a water-cooled condenser which removes all of the water vapor by cooling the stream below 100° C. The condensate is collected in a trap below the condenser which is provided with an overflow to drain. This trap also provides a pressure relief for the gas stream when the path to the gas analyzer is blocked during calibration.

G. Carbon Dioxide Concentration Measurement

The gas stream from the condenser passes through a filter which removes dirt particles entrained in the stream and is followed by an integrating volume to smooth out random fluctuations in CO_2 concentration. The stream is then delivered to the gas analyzer.

The gas analyzer is a nondispersive infrared analyzer (NDIR) which measures the concentration of CO_2 in the gas stream by measuring the absorption of infrared energy over a given path length in the gas stream at a wavelength selected to correspond with a principal abosrption band for CO_2.

By proper choice of oxygen flow rate and NDIR Analyzer sensitivity, the NDIR output signal can be calibrated in terms of the amount of organic carbon in the original sample.

I. Range Flexibility

Full-scale range of the stormwater TOC can be changed within limits by a change of NDIR analyzer sensitivity, oxygen flow rate, or sample flow rate, or a combination of the three.

III. DESIGN OBJECTIVES

A. Calibration

Calibration of the stormwater TOC is accomplished by using the auto-zero/auto-span accessory available from MSA. In this case, available oxygen is used as the zero gas and span gas must be provided and installed as specified by the manufacturer.

B. Alarms

If an operative failure should occur so as to result in a no-sample-delivery condition, this should be indicated by a temperature sensor at the reactor exit and be indicated by a low temperature signal. If a failure should occur in the sample delivery cooling jacket so as to deliver a large amount of cooling water to the reactor, this shall be detected by a high temperature signal. A thermocouple sensor connected to a meter relay shall be used to sound an alarm and turn on a light, which will indicate the problem with the instrument during operation.

C. Protective Devices

A high-pressure sensor rated to operate at 5 psi shall be installed in the oxygen delivery system so as to remove power from the pump if the pressure inside the reactor exceeds the preset value.

In the event of electrical failure of any of the operating components, a circuit breaker will operate to remove all power from the operating components.

D. Reactor Cleaning and Repacking

The combustion reactor assembly will be designed to permit removal, disassembly, cleaning, repacking, reassembly, and reinstallation in the unit within a period of 2 hours after the reactor temperature has cooled to a safe handling level, by a trained service technician. Special tools required, if any, will be supplied with the unit and will be mounted for storage within the cabinet.

IV. PERFORMANCE SPECIFICATIONS

A. TOC Range (Standard)

The stormwater TOC shall operate in the range 0—1000 mg/liter.

B. Repeatability

±2% of full scale

1. Defined as twice the standard deviation of a statistical sample of 10 or more readings taken over a twenty-minute period.

C. Linearity

The stormwater TOC shall be linear to ±1% of full scale.

D. Accuracy

±2% of full scale.

E. Zero Drift

±1% of full scale in 24 hours.

F. Span Drift

±1% of full scale in 24 hours.

G. Noise

Less than 1% of full scale.

H. Transport Delay

Five minutes from introduction of sample at intake fitting until output signal rises to 10% of final value.

I. Rise Time

Five minutes for output signal to rise from 10% of final value to 90% of final value.

J. Response Time

Ten minutes from introduction of sample at intake fitting until output signal reaches 90% of final value.

K. Warmup Time on Installation

Two hours.

V. ELECTRICAL SPECIFICATIONS

A. Input Power

117 Vac ±10%, 60 Hz + Hz, 1 ϕ, 25 A.

B. Signal Output

0—5 Vdc, into 1,000 ohms minimum.

VI. MECHANICAL SPECIFICATIONS

A. Overall Size and Weight (Approximate)

Height: 70 inches (178 cm) + 24 inches (61 cm) for auto-zero
Width: 29 inches (74 cm) + 12 inches (30.5 cm) for homogenizer
Depth: 26 inches (66 cm) + 9 inches (22.9 cm) for controller
Weight: 575 lb.

B. Mounting

The TOC unit is provided with an integral caster base for floor mounting and convenient handling during installation and service. Clearances required when installed: The auto-zero will be bracket-mounted.

Front: 25 inches Min (64 cm)
Rear: 10 inches Min (26 cm)
Sides: 12 inches Min (31 cm) for homogenizer and manifold

C. Accessibility

All routine service and calibration may be performed from the front of the unit. Internal components in the lower and central chambers of the unit are reached through two hinged access doors provided with safety locks. The NDIR analyzer is mounted behind a fixed upper panel, and withdraws from the front for service. The strip chart recorder is also mounted on this upper panel, and also withdraws from the front for service.

D. Cabinet Classification

The cabinet is designed for general purpose indoor installation, equivalent to NEMA type 1. It is not drip proof, dust tight, or weatherproof. When installations requiring these properties are made, the unit must be housed or enclosed in a manner sufficient to buffer the unit from the severe service conditions.

E. Finish

Cabinet: Epoxy paint, with primer
Panels: Epoxy paint, with primer
All internal aluminum: Clear anodized.

F. Plumbing Connections

Plumbing connections for external services and drain are located on a panel at the left rear bottom of the unit. Swagelock bulkhead fittings (1/4 inch) are employed. An exterior manifold is provided made of PVC plumbing hardware to provide drainage for sample, water and drainage.

G. Electrical Connections

1. ac Power: An 8-foot type "SO" power cord will be supplied with the unit, providing three #12 conductors and a standard three prong grounded male plug. Strain relief will be provided at the point where the cord emerges from the cabinet. Spade lug terminations will be used at a barrier strip provided within the cabinet.

2. Signal and Control Wiring: An internal barrier strip will be provided for spade lug termination of all customer-installed signal and control cable.

VII. SAMPLE REQUIREMENTS

A. Suspended Solids

Up to 1000 mg/l, no particles larger than 1/4 inch in any dimension, may be passed through the homogenizer.

B. Flow Rate

6 cc/min to the TOC unit

Note

This flow rate represents the sample actually drawn into the TOC analyzer. Lines delivering sample to the system should provide sufficient flow to maintain at least 2 feet per second (60 cm per second) velocity, with excess sample being bypassed to drain. Flow through the homogenizer must be maintained at 4 gallons/hour (15 liter/hours)minimum.

C. Pressure

10 to 30 psig (700 to 2,100 gm/cm^2) using the homogenizer.

D. Temperature

32° F to 140± F (nonfreezing) (° to 60° C).

VIII. ADDITIONAL SERVICES REQUIRED

A. Oxygen

1. Pressure: Regulated to 16 to 24 psig (1,125 to 1,700 gm/cm^2)
2. Flow: Approx. 4 CFH to maintain sparge & combustion gas

B. Span Gas (If Required)

CO_2/N_2 mixture of appropriate concentrations, in internally-mounted cylinder.

1. Pressure: 5 to 15 psig (350 to 1050 gm/cm^2)
2. Flow: Approx. 300 cc/min when calibrating

C. Cooling Water

1. Pressure: 10 to 50 psig (700 to 3,500 gm/cm^2)
2. Flow: 3 to 6 gpm (11.4 to 23 liters/min)
3. Temperature: 90° F Max. (32° C Max)

D. Sulfuric Acid

10% H_2SO_4 by weight. Internal container provided.
Consumption: 0.05 cc/min.

E. Drain (gravity) 6 gpm

A persistaltic pump shall be provided to remove water from the sump at a flow rate of 5cc/min.

F. Calibration Solution

Provision for external delivery of calibration solutions shall be provided.

IX. CONTROLS AND INDICATORS

A. Front Panel

1. Unit OFF:	Indicator/Pushbutton
2. Unit Start-up:	Indicator/Pushbutton
3. Unit Operate:	Indicator/Pushbutton
4. NDIR ON/OFF:	Toggle
5. NDIR ON:	Indicator

B. Internal Panel

1. Lamp Test:	Pushbutton
2. Reactor Flush:	Pushbutton
3. Sparge Gas Flow:	Indicator/Controller
4. Carrier Gas Reg:	100 Turn Controller
5. Carrier Gas Flow:	Rotameter
6. Reactor Temp:	Meter, 0 - 2,000°

7. Reactor Temp Adj: Potentiometer (Knob)
8. High Temp Limit: Potentiometer (Knob)
9. Main Power On: Indicator
10. Heater Breaker Trip: Indicator

C. Other Internal

1. Main Power On/Off: Circuit Breaker
2. Heater On/Off: Circuit Breaker
3. Sample Tube Cooling: Needle Valve
4. Calibrate Valve: Manual Valve

X. ENVIRONMENTAL

A. Ambient Temperature

32° F to 104° F (nonfreezing): (0° - 40° C)

B. Humidity

0 - 95% RH noncondensing

C. Vibration and Shock

Capable of withstanding normal shock and vibration in shipping.

XI. SAFETY PROVISIONS

A. Circuit breakers on Main ac and Heater ac.

B. Primary ac Fuses on power supply

C. High Voltage notices and shields on all terminal over 30 Vdc and 30 Vac.

D. Separate ground lug on rear of cabinet.

E. ac leakage current is less than 0.5 mA when measured at 115 Vac, 60 Hz.

F. High temperature notices on all hot surfaces over 55° C.

G. Dangerous chemical notice on inside of door.

H. Flush procedure instruction card on inside of lower swing-out door.

I. Automatic alarm and action provisions, as follows:

Condition	Possible Cause	Action
High Reactor Temp	1. Faulty thermocouple 2. Solid state relay failure 3. Faulty temperature controller	Complete instrument shut-down
High Reactor Pressure	1. Reactor plug 2. Input tube plug	Switch to Start-Up Mode (reactor heat maintained)
Loss of Reactor Cooling Water	1. Main water shut off 2. Hose leak 3. Faulty hose clamps	Complete shutdown
High Internal Instrument Temp	1. Reactor malfunction 2. Loss of cooling fans	Complete shutdown